OUTLINES OF THEORETICAL CHEMISTRY

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THEORETICAL CHEMISTRY

BY

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FOURTH EDITION
REVISED AND PARTLY REWRITTEN

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To

E. M. G.

WHOSE TENDER SYMPATHY HAS HELPED TO
LIGHTEN THE DARKNESS OF THE DAYS
DURING WHICH THESE PAGES
WERE WRITTEN

"I look upon the common operations and practices of chymists, almost as I do on the letters of the alphabet, without whose knowledge 'tis very hard for a man to become a philosopher; and yet that knowledge is very far from being sufficient to make him one."

ROBERT BOYLE. (*The Sceptical Chymist.*)

PREFACE TO FOURTH EDITION

Upon undertaking the preparation of a fourth edition of his "Outlines of Theoretical Chemistry," the author found himself confronted with the difficult problem of bringing the book thoroughly up to date without, at the same time, enlarging it to such an extent as to make it too voluminous for the use of colleges, or technical schools, where the time allotted to the study of physical chemistry is necessarily limited. In order to make room for new material it has been necessary to delete, or greatly abbreviate, certain sections of the preceding edition; in fact, Chapter XX, treating of the classification of the elements, has been wholly omitted. In order to preserve the original order of presentation of the subject, new material has been introduced, as far as possible, by expansion of the closely related sections of the former text.

Among the more important changes to be noted in the present edition, the following may be mentioned: — A fuller treatment of limiting densities and vapor pressures; a brief description of the latest and most accurate method of measuring heats of vaporization; a more comprehensive treatment of crystal structure and the methods of X-ray analysis; an enlargement of the section treating of the absorption of light and its bearing on chemical constitution; a thorough revision of the chapter on the elementary principles of thermodynamics; a more discriminating treatment of the phenomena of osmosis; the inclusion of the concepts of fugacity and activity in connection with the subject of vapor pressures of dilute solutions; a fuller discussion of the theories of emulsification and gel formation; an enlargement of the sections devoted to adsorption and the methods of preparation of colloids; a more detailed account of the theories of catalysis; the treatment of the more important practical applications of conductance and electrometric methods in separate sections in the respective chapters devoted to electrical conductance and electromotive force; the simplification of the treatment of hydrolysis; the adoption of a uniform and consistent system for the representation of galvanic cells, thereby connecting their polarity with the direction of cur-

rent-flow; a fuller treatment of both the hydrogen electrode and oxidation and reduction cells; the rearrangement and enlargement of the chapter on electrolysis and polarization; a brief presentation of the quantum theory together with its application to the principle of photochemical equivalence; an outline of Baly's fascinating and suggestive researches in the field of photosynthesis; and lastly, the complete revision of the chapter on atomic structure.

It is hoped that the foregoing changes may meet with the general approval of both teachers and students. Someone has said that "A book is of value for what we can get out of it, which is often better and finer than what the author put into it." Aware as he is of the imperfections which still inhere in this new edition notwithstanding the effort which has been made to remove them, the author will be more than gratified if any student who desires to gain a good working knowledge of physical chemistry can garner from this book the information he desires.

Again the author finds himself indebted to a number of friends for constructive criticisms and helpful suggestions. To all of these he would express his most sincere thanks.

For the splendid photographs of X-ray spectra of crystals which have been generously supplied by Dr. Ralph G. Wyckoff of the Geophysical Laboratory of Washington, D. C., the author is more than grateful.

Acknowledgment also is made to Adam Hilger, Ltd., and to Leeds and Northrup for the reproduction of cuts from their catalogs.

In the preparation of the indices the author has been fortunate in having the able assistance of his wife and to her much credit is due for their accuracy and completeness.

To Professor J. H. Mathews and his associates in the chemical department of the University of Wisconsin the author is under obligation for valuable assistance both in the task of revision and in reading the proof.

In the correction of typographical errors the able assistance of the proof readers of the Technical Composition Company cannot be too highly appraised.

FREDERICK H. GETMAN.

HILLSIDE LABORATORY,
STAMFORD, CONN.
December 18, 1926.

PREFACE TO THIRD EDITION

THE author has gladly availed himself of the opportunity, afforded by the demand for a third edition of his "Outlines of Theoretical Chemistry," to subject the entire text to a thorough revision.

This undertaking has involved the rewriting of large portions of the preceding edition, the introduction of much new material based upon recent advances in the science of physical chemistry, and such changes in the arrangement of the various chapters as the logical presentation of the subject demands.

The criticisms and suggestions which have been offered by a number of teachers, who have used the former editions of the book with their classes, have proven most helpful in the arduous task of revision.

The author is especially indebted to Professor J. H. Mathews of the University of Wisconsin, whose assistance has been of inestimable value, not only in connection with the revision of the text, but also during the period when the book was passing through the press. To Professor Farrington Daniels, also of the University of Wisconsin, the author is indebted for his help in reading the proof, while to Mr. Kenneth Tate, much credit is due for his assiduous care in the preparation of the indices. To all of those friends, who, by their generous coöperation, have very appreciably lightened his labors, the author would express his sincere gratitude.

FREDERICK H. GETMAN.

STAMFORD, CONN.
June 20, 1922.

EXTRACT FROM PREFACE TO SECOND EDITION

THE demand for a second edition of this book has not only afforded the author an opportunity to thoroughly revise the original text, but also has made it possible to include such new material as should properly find a place in an introductory text-book of theoretical chemistry.

The arduousness of the task of revision and amplification, has been appreciably lightened by the helpful criticisms and valuable suggestions, which have been received from those who have used the first edition with their classes.

So numerous were the additional topics suggested that the author found himself confronted with a veritable embarrassment of riches, and not the least difficult part of his task has been the attempt to weave in as many of these suggestions as seemed to be consistent with a well-balanced presentation of the entire subject.

The features which distinguish this edition from the preceding edition may be briefly summarized as follows: —

1. The necessity of introducing a short chapter on the modern conception of the atom and its structure, involved the further necessity of including a preliminary chapter, treating of those radioactive phenomena upon which the greater part of our present atomic theory is based.
2. The chapter on solids has been practically rewritten: the space formerly devoted to an outline of crystallography, being devoted, in the present edition, to a discussion of the absorption of heat by crystalline solids, and the bearing of X-ray spectra on crystalline form.
3. The increasing importance of colloidal phenomena, not only to the chemist, but also to the biologist, to the physician, and to the technologist, has made it seem desirable to rewrite the entire chapter devoted to the chemistry of colloids.
4. The Brownian movement, and its bearing upon the existence of molecules, has been briefly presented in a separate chapter, in order to emphasize the importance of

the brilliant experimental work of Perrin, and others, in confirming the kinetic theory.

5. The chapter treating of electromotive force has been enlarged, so as to include a discussion of some of the more valuable methods which have been proposed for determining junction potentials, and also to point out, several useful applications of concentration cells.
6. An entirely new chapter, in which an attempt has been made to present the salient facts and more important theories of photochemistry in succinct form, replaces the former chapter treating of the relations between radiant and chemical energy.

FREDERICK H. GETMAN.

STAMFORD, CONN.
Aug. 7, 1918.

EXTRACT FROM PREFACE TO FIRST EDITION

"The last thing that we find in making a book is to know what we must put first." — PASCAL.

THE present book is designed to meet the requirements of classes beginning the study of theoretical, or physical chemistry. A working knowledge of elementary chemistry and physics has been presupposed in the presentation of the subject, the introductory chapter being the only portion of the book in which space is devoted to a review of principles with which the student is assumed to be already familiar. With the exception of a few paragraphs in which the application of the calculus is unavoidable, no use is made of the higher mathematics, so that the book should be intelligible to the student of very moderate mathematical attainments. Wherever the calculus has been employed, the student who is unfamiliar with this useful tool must accept the correctness of the results, without attempting to follow the successive operations by which they are obtained.

The contributions to our knowledge in the domain of physical chemistry have increased with such rapidity within recent years, that the prospective author of a general text-book finds himself confronted with the vexing problem, of what to omit rather than what to include. In selecting material for this book, the author has been guided, in large measure, by his own experience in teaching theoretical chemistry to beginners, and to advanced students. The attempt has been made to present the more difficult portions of the subject, such as the osmotic theory of solutions, the laws of equilibrium and chemical action, and the principles of electrochemistry, in a clear and logical manner. While the treatment of each topic is necessarily brief, yet the effort has been made to avoid the sacrifice of clearness to brevity.

The author is fully convinced from his own experience, as well as from that of his colleagues, that the complete mastery of the fundamental principles of the science, is best attained through the solution of numerical examples. For this reason, typical

problems have been appended to various chapters of the book.

Numerous references to original papers have been given throughout, since the importance of literary research, on the part of the student, is conceded by all teachers to be of prime importance.

FREDERICK H. GETMAN.

STOCKBRIDGE, MASS.
Aug. 18, 1913.

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THEORETICAL CHEMISTRY

CHAPTER I

FUNDAMENTAL PRINCIPLES

Theoretical Chemistry. That portion of the science of chemistry which has for its object the study of the laws controlling chemical phenomena is called theoretical or physical chemistry. The first attempt to summarize the more important facts and ideas underlying the science of chemistry was made by Dalton in 1808 in his "New System of Chemical Philosophy." The birth of the new science of Theoretical Chemistry may be said to date from the appearance of Dalton's epoch-making book.

Theoretical chemistry is concerned with the great generalizations of chemical science and bears the same relation to chemistry that philosophy bears to the whole body of scientific truth; it aims to systematize all of the established facts of chemistry and to discover the laws governing the various phenomena of chemical action.

Law, Hypothesis, and Theory. The science of chemistry is based upon experimentally established facts. When a number of facts have been collected and classified we may proceed to draw inferences as to the behavior of systems under conditions which have not been investigated. This process of reasoning by analogy we term generalization and the conclusion reached we call a *law*. It is apparent that a law is not an expression of an infallible truth, but it is rather a condensed statement of facts which have been discovered by experiment. It enables us to predict results without recourse to experiment. The fewer the number of cases in which a law has been found to be invalid, the greater becomes our confidence in it, until eventually it may come to be regarded as tantamount to a statement of fact.

Natural laws may be discovered either by the correlation of experimentally determined facts, as outlined above, or by means of a

speculation as to the probable cause of the phenomenon in question. Such a speculation in regard to the cause of a phenomenon is called an *hypothesis*.

After an hypothesis has been subjected to the test of experiment and has been shown to apply to a large number of closely related phenomena it is termed a *theory*.

In his address to the British Association (Dundee, 1912), Professor Senier has this to say: "While the method of discovery in chemistry may be described generally, as inductive, still all the modes of inference which have come down to us from Aristotle, analogical, inductive, and deductive, are freely used. An hypothesis is framed which is then tested, directly or indirectly, by observation and experiment. All the skill, and all the resource the inquirer can command, are brought into his service; his work must be accurate; and with unqualified devotion to truth he abides by the result, and the hypothesis is established, and becomes a part of the theory of science, or is rejected or modified."

Elements and Compounds. All definite chemical substances are divided into two classes, *elements* and *compounds*.

Robert Boyle was the first to make this distinction. He defined an element as a substance which is incapable of resolution into anything simpler. The substances formed by the chemical combination of two or more elements he termed chemical compounds. This definition of an element as given by Boyle was later proposed by Lavoisier and, notwithstanding the vast accumulation of scientific knowledge since their time, the definition remains very satisfactory today.

At the present time we have a group of about ninety substances which have resisted all efforts to decompose them into simpler substances. These are the so-called chemical elements. It should be borne in mind, however, that because we have failed to resolve these substances into simpler forms of matter, we are not warranted in maintaining that such resolution may not be effected in the future.

Recent investigations of the radioactive elements have shown that they are continuously undergoing a series of transformations, one of the products of which is the inactive element helium. This behavior is contrary to the old view that transformation of one element into another is impossible. At first the attempt was made to explain it by assuming that the radioactive element was

a compound of helium with another element, but since the radioactive elements possess all of the properties characteristic of elements as distinguished from compounds, and find appropriate places in the periodic table of Mendeléeff, the "compound theory" must be abandoned. Uranium and thorium, the heaviest elements known, appear to be undergoing a process of spontaneous disintegration over which we have no control. The products of this disintegration have filled the gap in the periodic table between thorium and lead with about thirty new elements, each of which is in turn undergoing transformations similar to those of the parent elements. Professor Soddy* says: "In spite of the existence at one time of a vague belief (a belief which has no foundation), that all matter may be to a certain extent radioactive, just as all matter is believed to be to a certain extent magnetic, it is recognised today that radioactivity is an exceedingly rare property of matter."

Notwithstanding these remarkable discoveries, we may still hold to the idea of an element as suggested by Boyle and Lavoisier. Professor Walker says: "The elements form a group of substances, singular not only with respect to the resistance which they offer to decomposition, but also with respect to certain regularities displayed by them and not shared by substances which are designated as compounds."

Law of the Conservation of Mass. In 1774, as the result of a series of experiments, Lavoisier established the law of the conservation of mass which may be stated as follows: *In a chemical reaction the total mass of the reacting substances is equal to the total mass of the products of the reaction.* It is sometimes stated thus: — the total mass of the universe is a constant; but this form of statement is open to the objection that we have no means of verification; it is a statement of a fact which transcends our experience.

The law of the conservation of mass has been subjected to most rigid investigation by Landolt† in a series of experiments extending over a period of fifteen years.

The reacting substances, AB and CD, were placed in the two arms of the inverted U-tube shown in Fig. 1 which was then sealed at S and the whole weighed upon an extremely sensitive balance.

* Chemistry of the Radio-Elements, p. 2.

† Zeit. phys. chem., 12, 1 (1893); 55, 589 (1906).

The vessel was then inverted when the following reaction took place: —

$$AB + CD \rightarrow AD + CB.$$

When the reaction was complete and sufficient time had elapsed to allow the vessel to return to its original volume (this sometimes required nearly three weeks), it was weighed again, using every precaution to avoid errors, and any gain or loss in weight noted.

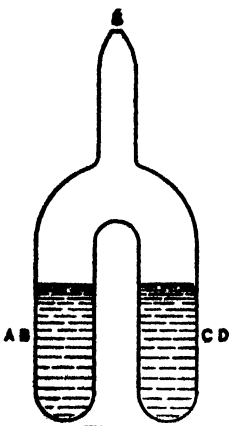

Fig. 1

Landolt concluded, from the thirty or more reactions which he studied, that the gain or loss in weight was less than one ten-millionth of the total weight.*

Law of Definite Proportions. The enunciation of the law of the conservation of mass and the introduction of the balance into the chemical laboratory marked the beginning of a new era in the history of chemistry, — the era of quantitative chemistry. As the result of painstaking experimental work, Richter and Proust announced the law of definite proportions about the beginning of the nineteenth century. This law may be expressed thus: *A definite chemical compound always contains the same elements united in the same proportion by weight.*

Shortly after the enunciation of this law its truth was questioned by the French chemist Berthollet.† From the results of a series of brilliant experiments, he became convinced that chemical reactions are largely controlled by the relative amounts of the reacting substances. As we shall see later, he really foreshadowed the work of Guldberg and Waage who were the first to correctly formulate the influence of mass on a chemical reaction. Berthollet argued that when two elements unite to form a compound, the proportion of one of the elements in the compound is conditioned solely by the amount of that element which is available. This led to the celebrated controversy between Berthollet and

* An excellent summary of this important investigation will be found in the Journal de Chimie physique, 6, 625 (1908). For later investigations on the conservation of mass, see paper by Manley, Phil. Trans. Roy. Soc. A 212, 227 (1913).

† Essai de statique chimique (1803).

Proust which finally resulted in the establishment of the latter's original statement. Subsequent investigation has only strengthened our faith in the law of definite proportions.

Law of Multiple Proportions. Elements are known to unite in more than one proportion by weight. Dalton analyzed the two compounds of carbon and hydrogen, methane and ethylene, and found that the ratio of the weights of carbon to hydrogen in the former was 6 : 2 while in the latter it was 6 : 1. That is, for the same weight of carbon, the weights of the hydrogen in the two compounds were in the ratio 2 : 1.

A large number of compounds were examined and similar simple ratios between the masses of the constituent elements were found. As a result of these observations, Dalton* formulated in 1808 the law of multiple proportions, as follows: *When two elements unite in more than one proportion, for a fixed mass of one element the masses of the other element bear to each other a simple ratio.* Notwithstanding the fact that Dalton was a careless experimenter, the subsequent investigations of Marignac and others have established the validity of his law.

Law of Combining Proportions. Dalton pointed out that it is possible to assign to every element a definite relative weight with which it enters into chemical combination. He observed that the weights, or simple multiples of the weights, of the different elements which unite with a given weight of a definite element, represent the weights of the different elements which combine with each other. The weights of the elements which combine with each other are termed their *combining weights.* This comprehensive law of chemical combination may be stated as follows: *Elements combine in the ratio of their combining weights, or in simple multiples of this ratio.* It will be observed that this law really includes the law of definite and the law of multiple proportions.

If we assume the combining weight of hydrogen to be unity, the combining weights of chlorine, oxygen and sulphur will be 35.5, 8 and 16 respectively. These numbers represent the ratios in which the elements substitute each other in chemical compounds. Hydrochloric acid, for example, contains 35.5 parts by weight of chlorine to 1 part by weight of hydrogen and when oxygen is substituted for chlorine, forming water, the new com-

* A New System of Chemical Philosophy (1808).

pound contains 8 parts by weight of oxygen to 1 part by weight of hydrogen. Similarly, if the oxygen be substituted by sulphur, forming hydrogen sulphide, there will be found 16 parts by weight of sulphur to 1 part by weight of hydrogen. We may say, then, that 35.5 parts of chlorine, 8 parts of oxygen and 16 parts of sulphur are *equivalent*.

A *chemical equivalent* may be defined as the weight of an element which is necessary to combine with, or displace, 1 part by weight of hydrogen.

The Atomic Theory. In very early times two different views were entertained by opposing schools of Greek philosophers as to the mechanical constitution of matter. According to the school of Plato and Aristotle, matter was thought to be continuous within the space it appears to fill and to be capable of indefinite subdivision. According to the other school, first taught by Leucippus, and afterwards by Democritus and Epicurus, matter was considered to be made up of primordial, extremely minute particles, distinct and separable from each other but in themselves incapable of division. These ultimate particles were called *atoms* (ἄτομος), signifying something indivisible. While the Aristotelian doctrine held sway for many centuries yet the notion of atoms was revived at intervals. Late in the seventeenth century, Boyle seems to have looked upon chemical combination as the result of atomic association.

Guided by these early speculations as to the constitution of matter and influenced by his study of the writings of Sir Isaac Newton, Dalton seems to have formed a mental picture of the part played by atoms in the act of chemical combination. After a few carelessly performed experiments, the results of which accorded with his preconceived ideas, he formulated his atomic theory.

According to this theory matter is composed of extremely minute, indivisible particles or atoms. Atoms of the same element are all of equal weight, but atoms of different elements have weights proportional to their combining numbers. Chemical compounds are formed by the union of atoms of different kinds. This theory offers a simple, rational explanation of the laws of chemical combination.

Since a chemical compound results from the union of atoms, each of which has a definite weight, its composition must be in-

variable, — which is the law of definite proportions. Again, when atoms combine in more than one proportion, for a fixed weight of atoms of one kind, the weights of the other species of atoms must bear to each other a simple ratio, since the atoms are indivisible units. This is clearly the law of multiple proportions.

Finally, the law of combining weights is seen to follow as a necessary consequence of the atomic theory, since the experimentally determined combining weights bear a simple relation to the relative weights of the atoms.

At the time when Dalton proposed his atomic theory, the number of facts to be explained was comparatively small, but with the enormous growth of the science of chemistry during the past century and with the vast accumulation of data, the theory has proved capable of affording adequate representation of all of the facts, and has opened the way to many important generalizations.

While the atomic theory has played a very important part in the development of modern chemistry, and while we recognize that it helps to clarify our thinking and enables us to construct a mental image of tiny spheres uniting to form a chemical compound, yet we must not forget the fact that these atoms are purely hypothetical.

Faraday has said: "Whether matter be atomic or not, this much is certain, that granting it to be atomic, it would appear as it now does."

Combining Weights and Atomic Weights. The problem of determining the relative atomic weights of the elements would at first sight appear to be a very simple matter. This might apparently be accomplished by selecting one element, say hydrogen, it being the lightest known element, as the standard; a compound of hydrogen and another element may then be analyzed and the amount of the other element in combination with one part by weight of hydrogen determined. This weight will be its atomic weight *only* when the compound contains but one atom of each element. To determine the relative atomic weight, therefore, we must know, in addition to the chemical equivalent of the element, the number of atoms present in the compound. For example, the analysis of water shows it to contain 8 parts by weight of oxygen to 1 part by weight of hydrogen; the chemical equivalent of oxygen is, therefore, 8, and if water contained but one atom of

hydrogen the atomic weight of oxygen would be 8. It can be shown, however, that water contains two atoms of hydrogen and one atom of oxygen, therefore, the atomic weight of oxygen must be 16. It is evident, therefore, that neither the analysis nor the synthesis of a compound is sufficient to enable us to determine the number of atoms of an element combined with one atom of hydrogen. We shall proceed to the consideration of the methods by which this problem may be solved.

Gay-Lussac's Law of Volumes. Gay-Lussac, in 1808, while studying the densities of gases before and after reaction, announced the following law: *When gases combine they do so in simple ratios by volume, and the volume of the gaseous product bears a simple ratio to the volumes of the reacting gases when measured under like conditions of temperature and pressure.* Thus, one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid; one volume of oxygen combines with two volumes of hydrogen to form two volumes of water (vapor); and one volume of nitrogen combines with three volumes of hydrogen to form two volumes of ammonia.

In a previous investigation, Gay-Lussac had shown that all gases behave identically when subjected to changes of temperature and pressure. This fact, taken together with the simple volumetric relation just enunciated and the atomic theory, suggested a possible relation between the number of ultimate particles in equal volumes of different gases.

Berzelius attempted to show that under corresponding conditions of temperature and pressure, equal volumes of different gases contain the same number of atoms, but he was compelled to abandon the assumption as untenable.

Avogadro's Hypothesis. It remained for the Italian physicist, Avogadro,* in 1811, to point out the distinction between atoms and molecules, terms which had been used almost synonymously up to his time. He defined the *atom* as the smallest particle which can enter into chemical combination, whereas the *molecule* is the smallest portion of matter which can exist in a free state. He then formulated the following hypothesis:† *Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules.* This hypothesis has been

* Jour. Phys. 73, 58 (1811).

† Ampere advanced practically the same hypothesis in 1814.

subjected to such rigid experimental and mathematical tests that its validity cannot be questioned.

Avogadro's Hypothesis and Molecular Weights. According to Gay-Lussac, when hydrogen and oxygen unite to form water vapor, two volumes of hydrogen combine with one volume of oxygen yielding two volumes of water vapor. According to the hypothesis of Avogadro, the number of molecules of water vapor is double the number of molecules of oxygen, and, since each molecule of water vapor must contain at least one atom of oxygen, it follows that the molecule of oxygen must contain at least two atoms of oxygen. Since the value of the atomic weight of oxygen is 16, it is evident that its molecular weight must be 32.

It is convenient to express molecular and atomic weights in terms of the same unit, for then the molecular weight of a substance will be simply the sum of the weights of the atoms contained in the molecule. The determination of the approximate molecular weight of a substance, therefore, resolves itself into ascertaining the mass of its vapor in grams which, under the same conditions of temperature and pressure, will occupy the same volume as 32 grams of oxygen.

This weight is called the *gram-molecular weight* or the *molar weight* of the substance, while the corresponding volume is known as the *gram-molecular* or *molar volume*. It is nearly the same for all gases, and at 0° and 760 mm. it may be taken equal to *22.4* liters. The molecular weights obtained from vapor density measurements are approximate only, because of the failure of most gases and vapors to obey the simple gas laws, a condition essential to the strict applicability of Avogadro's hypothesis.

Atomic Weights from Molecular Weights. While vapor density determinations as ordinarily carried out do not give exact molecular weights, it is an easy matter to arrive at the true values when we take into consideration the results of chemical analysis. It is apparent that the true molecular weight must be the sum of the weights of the constituent elements, these weights being exact multiples or submultiples of their combining proportions, which proportions have been determined by analysis alone. We select, as the true molecular weight, the value which is nearest to the approximate molecular weight calculated from the vapor density of the substance. For example, the molecular weight of ammonia, as computed from its vapor density, is 17.5 or, in other words,

17.5 grams of ammonia occupy the same volume as 32 grams of oxygen, measured under the same conditions of temperature and pressure. The analysis of ammonia shows us that for every gram of hydrogen, there are present 4.67 grams of nitrogen. Hence the true molecular weight must contain a multiple of 1 gram of hydrogen and the same multiple of 4.67 grams of nitrogen. The problem is, to find what integral value must be assigned to x in the expression, $x\ (1 + 4.67)$, in order that it may give the closest approximation to 17.5. Clearly if $x = 3$ the value of the expression becomes 17, and this we take to be the true molecular weight. This gives $3 \times 4.67 = 14$ as the probable atomic weight of nitrogen. To decide whether the atomic weight of nitrogen is a multiple or a submultiple of 14, we must determine the molecular weights of a large number of gaseous or vaporisable compounds of nitrogen, and select as the atomic weight the smallest quantity of the element which is present in any one of them.

The following table gives a list of seven gaseous compounds of nitrogen together with their gram-molecular weights, and the number of grams of the element in the gram-molecule.

Compound	Gram-mol. Wt.	Grams Nitrogen.
Ammonia	17	14
Nitric oxide	30	14
Nitrogen peroxide	46	14
Methyl nitrate	77	14
Cyanogen chloride	61.5	14
Nitrous oxide	44	28
Cyanogen	52	28

It will be observed that the least weight of nitrogen entering into a gram-molecular weight of any of these compounds is 14 grams, and, therefore, we accept this value as the atomic weight of the element, although there is still a very slight chance that in some other compound of nitrogen a smaller weight of the element may be found. We shall now proceed to point out that there are methods by which the probable values of the atomic weights may be checked.

Specific Heat and Atomic Weight. In 1819, the French chemists, Dulong and Petit,* pointed out a very simple relation be-

* Ann. Chim. Phys., 10, 395 (1819).

tween the specific heats of the elements in the solid state and their atomic weights. This relation, known as the law of Dulong and Petit, is as follows: *The product of the specific heat and the atomic weight of the solid elements is constant.* The value of this constant, called the *atomic heat,* is approximately 6.4. A little reflection will show that an alternative statement of this law is that *the atoms of the elements in the solid state have the same thermal capacity.* The specific heats, atomic weights and atomic heats of several elements are given in the subjoined table.

ATOMIC HEATS

Element.	At. Wt.	Sp. Ht.	At. Ht.
Lithium	7	0.940	6.6
Glucinum	9	0.410	3.7
Boron (amorphous)	11	0.250	2.8
Carbon (diamond)	12	0.140	1.7
Sodium	23	0.290	6.7
Silicon (crystalline)	28	0.160	4.5
Potassium	39	0.166	6.5
Calcium	40	0.170	6.8
Iron	56	0.112	6.3
Copper	63	0.093	5.9
Zinc	65	0.093	6.1
Silver	108	0.056	6.0
Tin	119	0.054	6.5
Gold	197	0.032	6.3
Mercury	200	0.032	6.4

It is truly remarkable that elements differing as greatly as lithium and mercury, not only in atomic weight but in other properties as well, should have nearly identical atomic heats. It will be observed that the atomic heats of boron, silicon, carbon and glucinum are too low. This departure from the law of Dulong and Petit is more apparent than real, for in the statement of the law there is no specification as to the temperature at which the specific heat should be determined. The specific heats of all solids vary with the temperature, this variation being greater in the case of some elements than in that of others. It has been shown that the specific heats of the above four elements increase rapidly with rise of temperature and approach limiting values. As these values are approached the product of specific heat and atomic weight approximates more and more closely to the mean value of the constant, 6.4.

The following table gives the values obtained by Weber* for carbon and silicon.

VARIATION OF ATOMIC HEAT WITH TEMPERATURE

CARBON (DIAMOND)

Temperature, degrees.	Sp. Ht.	At. Ht.
−50	0.0635	0.76
+10	0.1128	1.35
85	0.1765	2.12
206	0.2733	3.28
607	0.4408	5.30
806	0.4489	5.40
985	0.4589	5.50

CARBON (GRAPHITE)

Temperature, degrees.	Sp. Ht.	At. Ht.
−50	0.1138	1.37
+10	0.1604	1.93
61	0.1990	2.39
202	0.2966	3.56
642	0.4454	5.35
822	0.4539	5.45
978	0.4670	5.50

SILICON

Temperature, degrees.	Sp. Ht.	At. Ht.
−40	0.136	3.81
+57	0.183	5.13
129	0.196	5.50
232	0.203	5.63

It is evident that this empirical relation can be used to determine the approximate atomic weight of an element when its specific heat is known, thus

$$\text{atomic weight} = \frac{6.4}{\text{specific heat}}. \qquad (1)$$

The law of Dulong and Petit has been of great service in fixing and checking atomic weights.

About twenty years after the law of Dulong and Petit was

* Pogg. Ann., 154, 367 (1875).

formulated, Neumann* showed that a similar relation holds for compounds of the same general chemical character. Neumann's law may be stated thus: *Similarly constituted compounds in the solid state have the same molecular heat.* Subsequently Kopp† pointed out that *the thermal capacity of the atoms is not appreciably altered when they enter into chemical combination*, or in other words, the molecular heat of solid compounds is an additive property, being made up of the atomic heats of the constituent elements.

For example, the specific heat of $PbBr_2$ is 0.054 and its molecular weight is 366.8; therefore, the molecular heat is $0.054 \times 366.8 = 19.9$. Since there are three atoms in the molecule, $19.9 \div 3 = 6.6$ is their average atomic heat, a value in excellent agreement with the constant in the law of Dulong and Petit. Neumann's law may be used to estimate the atomic heats of elements which cannot be readily investigated in the solid state. The following table gives a list of atomic heats of elements in the solid state derived by means of Neumann's law.

DERIVED ATOMIC HEATS

Element.	At. Ht.	Element.	At. Ht.
Hydrogen	2.3	Carbon	1.8
Oxygen	4.0	Silicon	4.0
Fluorine	5.0	Phosphorus	5.4
Nitrogen	5.5	Sulphur	5.4

Isomorphism. From a study of the corresponding salts of phosphoric and arsenic acids, Mitscherlich‡ observed that they crystallise with the same number of molecules of water and are nearly identical in crystalline form, it being possible to obtain *mixed crystals* from solutions containing both salts. This suggested to Mitscherlich a line of investigation which resulted, in 1820, in the establishment of the law of isomorphism which bears his name.

This law may be stated as follows: *An equal number of atoms combined in the same manner yield the same crystal form, which is independent of the chemical nature of the atoms and dependent upon*

* Pogg. Ann., 23, 1 (1831).
† Lieb. Ann. (1864), Suppl., 3, 5.
‡ Ann. Chim. Phys. (2), 14, 172 (1820).

their number and position. Thus, when one element replaces another in a compound without changing its crystalline form, Mitscherlich assumed that one element has displaced the other, atom for atom. For example, having two isomorphous substances, such as $BaCl_2.2\,H_2O$ and $BaBr_2.2\,H_2O$, we assume that the bromine in the second compound has replaced the chlorine in the first and, if the atomic weights of all of the elements in the first compound are known, then it is evident that the atomic weight of the bromine in the second compound can be easily calculated. This method was largely used by Berselius in fixing atomic weights and in checking the values obtained by the volumetric method. It should be remembered that the converse of the law of isomorphism does not hold, since elements may replace each other, atom for atom, without preserving the same form of crystallization. Many exceptions to the law have been pointed out. For example, Mitscherlich himself showed that Na_2SO_4 and $BaMn_2O_8$ are isomorphous and yet the two molecules do not contain the same number of atoms. Furthermore, careful measurements of the interfacial angles of crystals have revealed the fact, that substances which have been regarded as isomorphous are only approximately so; thus the interfacial angles of the apparently isomorphous crystalline salts $MgSO_4.7\,H_2O$, $ZnSO_4.7\,H_2O$ and $NiSO_4.7\,H_2O$ are found to be 89° 26′, 88° 53′ and 88° 56′, respectively. Ostwald has suggested that the term *homeomorphous* be applied to designate substances which have nearly identical form. At best the principle of isomorphism is only an approximation and should be employed with caution.

Valence. During the latter half of the nineteenth century the usefulness of the atomic theory was greatly enhanced by the introduction of certain assumptions concerning the combining power of the atoms. These assumptions, constituting the so-called doctrine of *valence*, were forced upon chemists in order that a satisfactory explanation might be offered of the phenomenon of isomerism. A consideration of the following formulas, — HCl, H_2O, NH_3, CH_4, — shows that the power to combine with hydrogen increases regularly from chlorine, which combines with hydrogen, atom for atom, to carbon, one atom of which is capable of combining with four atoms of hydrogen. Either hydrogen or chlorine, each of which is capable of combining with but one atom of the other, may be taken as an example of the simplest

kind of atom. Any element like hydrogen or chlorine is called a *univalent* element, whereas elements similar to oxygen, nitrogen and carbon, which are capable of combining with two, three or four atoms of hydrogen, are called *bivalent*, *trivalent*, and *quadrivalent* elements respectively. Most elements belong to one or the other of these four classes, although *quinquivalent*, *sexivalent* and *septivalent* elements are known. The familiar bonds or linkages of structural formulas are graphic representations of the valence of the atoms constituting the molecule. This useful conception of valence has made possible the prediction of the properties of many compounds before they have been discovered in nature or in the laboratory.

Atomic Weights. Among the first to recognize the importance of Dalton's atomic theory was the Swedish chemist, Berzelius. He foresaw the importance for chemists of a table of exact atomic weights, and in 1810 he undertook the task of determining the combining weights of most of the known elements. For nearly six years he was engaged in determining the exact composition of a large number of compounds and calculating the combining weights of their constituent elements, thus compiling the first table of atomic weights.

Numerous investigators since Berzelius have been engaged in this important work, among whom should be mentioned Stas, Marignac, Morley and Richards. On two occasions special stimulus was given to such investigations. The first occasion was in 1815, when Prout suggested that the atomic weights of the elements are exact multiples of the atomic weight of hydrogen. The values obtained by Berzelius were incompatible with the hypothesis of Prout, although the atomic weights of several of the elements differed but little from integral values. To test the accuracy of this hypothesis, Stas undertook the determination of the atomic weights of several elements with a degree of accuracy such that his maximum experimental error was less than the difference between the atomic weight found and the nearest whole number. This important series of investigations disproved Prout's hypothesis as originally stated. The second occasion when the investigation of atomic weights received a special impulse, was in 1869, when Mendeléeff brought forward the periodic classification of the elements. When the elements were arranged in the order of their atomic weights, several of them were found to fall in groups

ciple is known to be strictly true for ideal gases only, it has been shown by D. Berthelot and others that, if due allowance is made for the compressibility of a gas, the experimentally determined value of its density may be corrected so as to render possible the calculation of the exact value of the molecular weight of the gas. Making use of this so-called method of "limiting densities," Gray* has determined the atomic weight of nitrogen with great precision. Instead of using nitrogen itself, however, he found it more convenient to employ nitric oxide. This gas was prepared in a high state of purity and its density determined with the utmost care. The molecular weight of NO, as calculated from the corrected value of the density, was found to be 30.004; if we deduct from this the value of the atomic weight of oxygen, we have 30.004 − 16.000 = 14.004 as the value of the atomic weight of nitrogen.

The relative accuracy of the two methods for the determination of atomic weights has been carefully considered by Guye† who concludes that the results obtained by the physical method compare favorably with those obtained by the purely chemical method.‡

International Atomic Weights. Dalton selected hydrogen, the lightest known element, as the unit of his system of combining weights of the elements, but Berzelius pointed out that this was an unwise choice since but relatively few of the elements form stable compounds with hydrogen. He proposed, therefore, that oxygen should be taken as the standard, assigning to it the arbitrary value 100. This proposal of Berzelius, to substitute oxygen for hydrogen as the unit of atomic weights, did not receive serious consideration until quite recently, when the International Committee on Atomic Weights took up the matter and, after careful deliberation, decided in favor of the oxygen standard. The atomic weight of oxygen is taken as 16, and the unit to which all atomic weights are referred is one-sixteenth of this weight. The atomic weight of hydrogen on this basis is 1.008. Aside from the fact that most of the elements form compounds with oxygen which are suitable for analysis, the atomic weights of more of the elements approximate to integral values when oxygen instead of hydrogen is used as the standard.

The table on page 19 gives the values of the atomic weights

* Jour. Chem. Soc. 87, 1601 (1905). † Jour. Chim. Phys. 3, 352 (1905).

‡ The method of "limiting densities" will be more fully treated in a subsequent chapter. See p. 64.

as published by the International Committee on Atomic Weights for 1925.

International Table of Atomic Weights of the Chemical Elements. — 1925

	Symbol	At. No.	At. weight
Aluminium	Al	13	26·97
Antimony	Sb	51	121·77
Argon	A (Ar)	18	39·91
Arsenic	As	33	74·96
Barium	Ba	56	137·37
Beryllium / Glucinium	Be / Gl	4	9·02
Bismuth	Bi	83	209·00
Boron	B	5	10·82
Bromine	Br	35	79·916
Cadmium	Cd	48	112·41
Caesium	Cs	55	132·81
Calcium	Ca	20	40·07
Carbon	C	6	12·000
Cerium	Ce	58	140·25
Chlorine	Cl	17	35·457
Chromium	Cr	24	52·01
Cobalt	Co	27	58·94
Columbium / Niobium	Cb / Nb	41	93·1
Copper	Cu	29	63·57
Dysprosium	Dy	66	162·52
Erbium	Er	68	167·7
Europium	Eu	63	152·0
Fluorine	F	9	19·00
Gadolinium	Gd	64	157·26
Gallium	Ga	31	69·72
Germanium	Ge	32	72·60
Gold	Au	79	197·2
Helium	He	2	4·00
Holmium	Ho	67	163·4
Hydrogen	H	1	1·008
Indium	In	49	114·8
Iodine	I (J)	53	126·932
Iridium	Ir	77	193·1
Iron	Fe	26	55·84
Krypton	Kr	36	82·9
Lanthanum	La	57	138·90
Lead	Pb	82	207·20
Lithium	Li	3	6·940
Lutecium	Lu	71	175·0
Magnesium	Mg	12	24·32
Manganese	Mn	25	54·93
Mercury	Hg	80	200·61
Molybdenum	Mo	42	96·0
Neodymium	Nd	60	144·27
Neon	Ne	10	20·2
Nickel	Ni	28	58·69
Nitrogen	N	7	14·008
Osmium	Os	76	190·8
Oxygen	O	8	16·000
Palladium	Pd	46	106·7
Phosphorus	P	15	31·027
Platinum	Pt	78	195·23
Potassium	K	19	39·096
Praseodymium	Pr	59	140·92
Radium	Ra	88	225·95
Radon	Rn	86	222
Rhodium	Rh	45	102·91
Rubidium	Rb	37	85·44
Ruthenium	Ru	44	101·7
Samarium	Sm	62	150·43
Scandium	Sc	21	45·10
Selenium	Se	34	79·2
Silicon	Si	14	28·06
Silver	Ag	47	107·880
Sodium	Na	11	22·997
Strontium	Sr	38	87·63
Sulphur	S	16	32·064
Tantalum	Ta	73	181·5
Tellurium	Te	52	127·5
Terbium	Tb	65	159·2
Thallium	Tl	81	204·39
Thorium	Th	90	232·15
Thulium	Tm	69	169·4
Tin	Sn	50	118·70
Titanium	Ti	22	48·1
Tungsten / Wolfram	W	74	184·0
Uranium	U	92	238·17
Vanadium	V	23	50·96
Xenon	Xe	54	130·2
Ytterbium	Yb	70	173·6
Yttrium	Y	39	88·9
Zinc	Zn	30	65·38
Zirconium	Zr	40	91

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Les Travaux de l'Université de Harvard sur les Poids Atomiques. T. W. Richards. Journal de Chimie Physique, 6, 92 (1908).

PROBLEMS

1. Stas found on heating 498.6355 grams of potassium chlorate that the residue of potassium chloride weighed 303.3870 grams. Assuming that the atomic weights of oxygen and chlorine are 16 and 35.46 respectively, calculate the value of the atomic weight of potassium.

2. On burning 16.1920 grams of pure carbon, 59.3765 grams of carbon dioxide is obtained. If the atomic weight of oxygen is taken as 16, what is the value of the atomic weight of carbon?

3. Calculate the value of the atomic weight of barium from the following data: 100 grams of barium chloride yield 112.09 grams of barium sulphate; O = 16, S = 32.06, Cl = 35.46.

4. Erdmann and Marchand found on heating 13.6031 grams of calcium carbonate that the residue of calcium oxide weighed 7.6175 grams. What is the value of the atomic weight of calcium? (O = 16, C = 12).

5. The atomic weight of silver is 107.88 and its specific heat is 0.057. The specific heat of a metal M is found to be 0.0306 and the analysis of its chloride shows that 70 parts of the metal unite with 35.46 parts of chlorine. Find its atomic weight.

6. The specific heat of cadmium is 0.0567 and its equivalent is 56. Calculate its atomic weight.

7. Baxter and Grover in their determination of the atomic weight of lead found the ratio $PbCl_2/2\,Ag = 1.28905$. If the atomic weights of silver and chlorine are 107.880 and 35.457 respectively, calculate the value of the atomic weight of lead.

8. The weight of 1 liter of carbon dioxide as computed from the value of the limiting density is 1.9635 grams. Calculate the value of the atomic weight of carbon on the basis of O = 16.

9. The weight of 1 liter of sulphur dioxide as computed from the value of its limiting density is 2.8586 grams. Calculate the value of the atomic weight of sulphur.

10. The specific gravity of ammonia referred to oxygen is 0.53940. Calculate the approximate value of the atomic weight of nitrogen, having given the atomic weight of hydrogen, 1.008.

CHAPTER II

GASES

The Gas Laws. Matter in the gaseous state possesses the property of filling completely and to a uniform density any available space. Among the most pronounced characteristics of gases are lack of definite shape or volume, low density and small viscosity. The laws expressing the behavior of gases under different conditions are relatively simple and to a large extent are independent of the nature of the gas. The temperature and pressure coefficients of all gases are very nearly the same.

In 1662, Robert Boyle discovered the familiar law that *at constant temperature, the volume of a gas is inversely proportional to the pressure.* This may be expressed mathematically as follows: —

$$v \propto \frac{1}{p} \text{(temperature constant)},$$

where v is the volume and p the pressure.

In 1801, Gay-Lussac discovered the law of the variation of the volume of a gas with temperature.

This law may be formulated thus: — *At constant pressure, the volume of a gas is directly proportional to its absolute temperature,* or

$$v \propto T \text{ (pressure constant)}.$$

There are three conditions which may be varied, viz., volume, temperature and pressure. The preceding laws have dealt with the relation between two pairs of the variables when the third is held constant. There remains to consider the relation between the third pair of variables, pressure and temperature, the volume being kept constant. Evidently a necessary corollary of the first two laws is, that *at constant volume, the pressure of a gas is directly proportional to its absolute temperature,* or

$$p \propto T \text{ (volume constant)}.$$

These three laws may be combined into a single mathematical expression as follows: —

$$v \propto \frac{1}{p} \ (T \text{ const.}) \text{ law of Boyle,}$$

$$v \propto T \ (p \text{ const.}) \text{ law of Gay-Lussac;}$$

combining these two variations we have

$$v \propto \frac{T}{p},$$

or introducing a proportionality factor k,

$$v = k\frac{T}{p},$$

or

$$vp = kT. \tag{1}$$

If the temperature of the gas be 0° (273° absolute), and the corresponding volume and pressure, v_0 and p_0 respectively, then (1) becomes

$$v_0 p_0 = 273\, k,$$

and

$$k = \frac{v_0 p_0}{273}: \tag{2}$$

eliminating the constant k between (1) and (2), we have

$$vp = \frac{v_0 p_0}{273} T.$$

For a given amount of any one gas the term $\frac{v_0 p_0}{273}$ is a constant. If v_0 is the volume of 1 gram of gas at 0° and 76 cm., we write

$$vp = rT, \tag{3}$$

where v is the volume of 1 gram of gas at the temperature T and the pressure p, and r is a constant called the *specific gas constant.* On the other hand when v_0 denotes the volume of one mol of gas at 0° and 76 cm. (22.4 liters), the equation becomes

$$vp = RT, \tag{4}$$

where R is termed the *molar gas constant,* which has the same value for all gases. If M is the molecular weight of the gas, $Mr = R$. Equation (4) is the fundamental gas equation

Evaluation of the Molar Gas Constant. Since the product of p and v represents work, R must be expressed in energy units divided by temperature. There are four different units in which the molar gas constant is commonly expressed, viz., (1) gram-centimeters, (2) ergs, (3) calories, and (4) liter-atmospheres.

1. *R in gram-centimeters.* The volume, v, of 1 mol of gas at 0° and 76 cm. is 22.4 liters or 22,400 cc. The pressure, p, is 76 cm. multiplied by 13.59 (the density of mercury), or 1033.3 grams per square centimeter. Substituting we obtain

$$R = \frac{p_0 v_0}{T} = \frac{1033.3 \times 22{,}400}{273} = 84{,}760 \text{ grm. cms. per degree.}$$

2. *R in ergs.* To convert gram-centimeters into ergs we must multiply by the acceleration due to gravity, $g = 980.6$ cm. per sec., or

$$R = 84{,}760 \times 980.6 = 83{,}150{,}000 \text{ ergs per degree.}$$

3. *R in calories.* To express work in terms of heat, we must divide by the mechanical equivalent of heat, or, since 1 calorie is equivalent to 42,640 gr. cm. or 41,830,000 ergs, we have

$$R = \frac{83{,}150{,}000}{41{,}830{,}000} = 1.99 \text{ cals. per degree (approximately 2 cals. per degree).}$$

4. *R in liter-atmospheres.* A liter-atmosphere may be defined as the work done by 1 atmosphere on a square decimeter through a decimeter. If p_0 is the pressure in atmospheres, and v_0 is the volume in liters, we have

$$R = \frac{p_0 v_0}{T} = \frac{22.4}{273} = 0.0821 \text{ liter-atmosphere per degree.}$$

Avogadro's Constant. Several recent experimental investigations have furnished the necessary data for the calculation of the actual number of molecules contained in one gram-molecule of gas. This number has been called the *Avogadro constant* or *Avogadro number.* Notwithstanding the fact that a wide variety of experimental methods now exists upon which independent calculations of this constant can be based, it is interesting to note that the agreement of the results obtained by these different methods is exceedingly close. All of the methods which have been employed in the evaluation of Avogadro's constant have

been subjected to the most rigorous tests to insure their accuracy together with that of the calculations based thereon.

The following table gives a partial list of the values of the Avogadro constant as determined by various observers using different

VALUE OF AVOGADRO'S CONSTANT

Observer.	Method.	No. Molecules in One Gram-molecule = $N \times 10^{23}$
Perrin	Brownian movement	6.8
Millikan	Determination of elemental electric charge	6.06 ± 0.001
Rutherford	Charge on α-particle	6.2
Boltwood	α-particles from radium	6.3
Curie	α-particles from polonium	6.5
King	Rate of fall of oil drops	6.03
Planck	Radiation	6.06

experimental methods. Of these different values, undoubtedly that due to Millikan in which the estimated error does not exceed 0.1 per cent is the most trustworthy.

It has been found that, under the most favorable conditions, the degree of rarefaction obtainable with a modern high-vacuum pump is such that the number of molecules per cubic centimeter is reduced to approximately 7×10^9. When this figure is compared with 2.705×10^{19}, the number of molecules present in one cubic centimeter of gas, the futility of attempting to produce a perfect vacuum is quite obvious.

Deviations from the Gas Laws. Careful experiments by Amagat* and others on the behavior of gases over extended ranges of temperature and pressure have shown that the fundamental gas equation, $pv = RT$, is not strictly applicable to any one gas, the deviations depending upon the nature of the gas and the conditions under which it is observed. It has been shown that the gas laws are more nearly obeyed the lower the pressure, the higher the temperature and the further the gas is removed from the critical state. A gas which would conform to the requirements of the fundamental gas equation is called an *ideal* or *perfect gas*. Almost all gases are far from ideal in their behavior.

* Ann. Chim. phys. (5) 19, 345 (1880).

At constant temperature the product, pv, in the gas equation is constant, so that if we plot pressures as abscissæ and the corresponding values of pv as ordinates, for an ideal gas we should

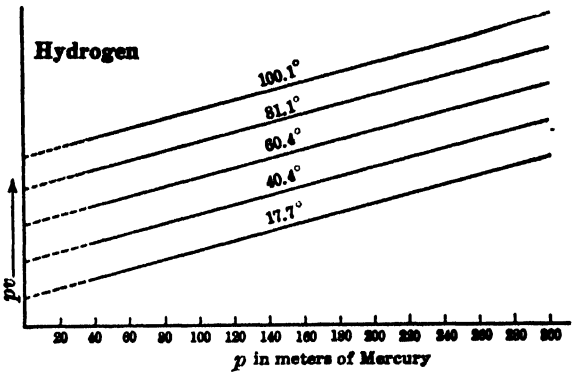

Fig. 2

obtain a straight line parallel to the axis of abscissæ. The results obtained with six typical gases are shown in the accompanying diagrams, Figs. 2 to 5. It will be apparent that all of these gases

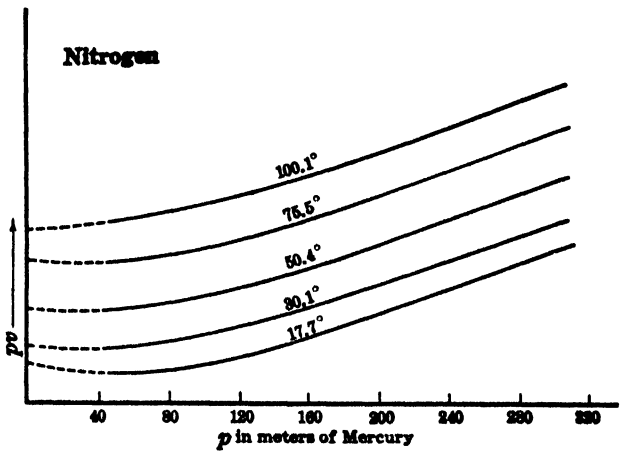

Fig. 3

depart widely from ideal behavior. In the case of hydrogen and neon pv increases continuously with the pressure, while with nitrogen and carbon dioxide it first decreases, attains to a minimum value and then increases with increasing pressure. Oxygen gives

a straight line sloping upwards to the pv axis, while helium gives a perfectly horizontal line. Although helium thus conforms to

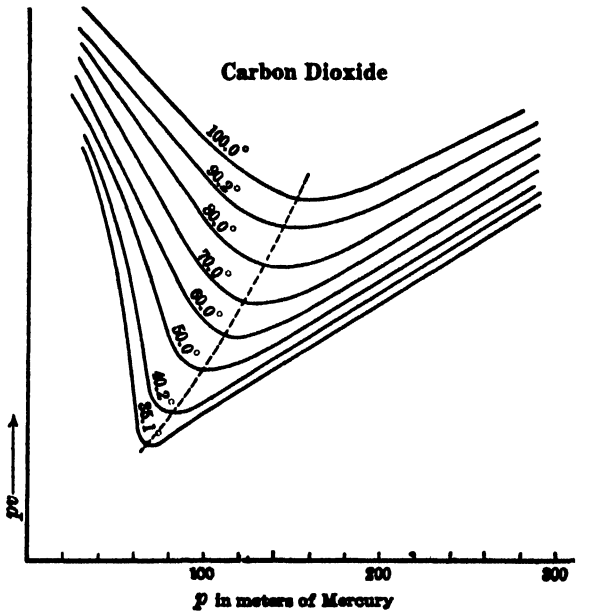

Fig. 4

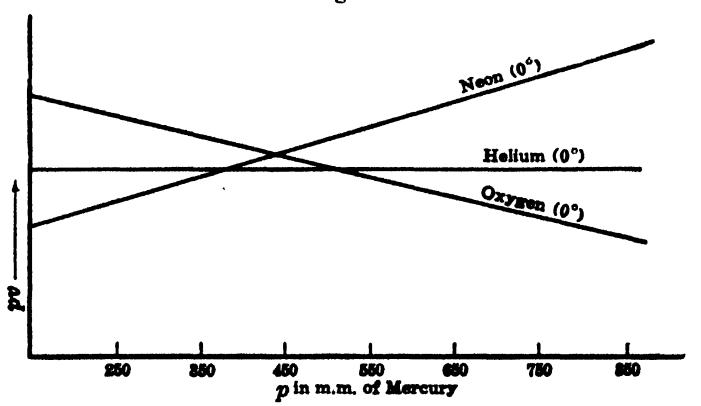

Fig. 5

Boyle's law at 0°, it fails to behave ideally at higher temperatures. With the exception of hydrogen, all gases show a minimum in the curve, thus indicating that at first the compressibility is greater than corresponds with the law of Boyle, but diminishes

continuously until, for a short range of pressure, the law is followed strictly; beyond this point the compressibility is less than Boyle's law requires.

Hydrogen is exceptional in that it is always less compressible than the law demands. This is true for all ordinary temperatures, but it is highly probable that at extremely low temperatures the curve would show a minimum. The two curves for carbon dioxide at 31°.5 and 100° illustrate the fact that the deviations from the gas laws become less as the temperature increases. The deviations of gases from the laws of Boyle and Gay-Lussac, as well as their behavior in general, may be satisfactorily accounted for on the basis of the kinetic theory.

Kinetic Theory of Gases. The first attempt to explain the properties of gases on a purely mechanical basis was made by Bernoulli in 1738. Subsequently, through the labors of Kroenig, Clausius, Maxwell, Boltzmann and others, his ideas were developed into what is known today as the kinetic theory of gases. According to this theory, gases are considered to be made up of minute, perfectly elastic particles which are ceaselessly moving about with high velocities, colliding with each other and with the walls of the containing vessel. These particles are identical with the molecules defined by Avogadro. The volume actually occupied by the gas molecules is supposed to be much smaller than the volume filled by them under ordinary conditions, thus allowing the molecules to move about free from one another's influence except when they collide. The distance through which a molecule moves before colliding with another molecule is known as its *mean free path.* In terms of this theory, the pressure exerted by a gas is due to the combined effect of the impacts of the moving molecules upon the walls of the containing vessel, the magnitude of the pressure being dependent upon the kinetic energy of the molecules and their number.

Derivation of the Kinetic Equation. Starting with the assumptions already made, it is possible to derive a formula by means of which the gas laws may be deduced. Imagine n molecules, each having a mass, m, confined within the cubical vessel shown in Fig. 6, the edge of which has a length, l. While the different molecules are doubtless moving with different velocities, there must be an average velocity for all of them. Let u denote this mean velocity of translation. The molecules will impinge upon

the walls in all directions but the velocity of each may be resolved according to the well-known dynamical principle into three components, x, y and z, parallel to the three rectangular axes, X, Y and Z. The analytical expression for the velocity of a single molecule, M, is

$$u^2 = x^2 + y^2 + z^2.$$

In words, this means that the effect of the collision of the molecule upon the wall of the containing vessel, is equivalent to the combined effect of successive collisions of the molecule perpendicular to the three walls of the cubical vessel with the velocities x, y and z respectively. Fixing our attention upon the horizontal component, the molecule will collide with the wall with a velocity x, and owing to its perfect elasticity it will rebound with a velocity $-x$, having suffered no loss in kinetic energy. The momentum before collision was mx and after collision it will be $-mx$, the total change in momentum being $2mx$. The distance between the two walls being l, the number of collisions on a wall in unit time will be x/l, and the total effect of a single molecule in one direction in unit time will be $2mx \cdot x/l = 2mx^2/l$. The same reasoning is applicable to the other components, so that the combined action of a single molecule on the six sides of the vessel will be

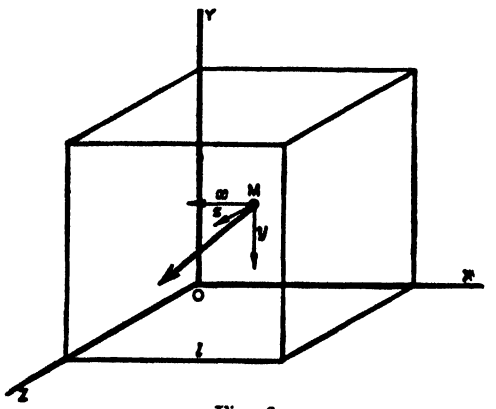

Fig. 6

$$\frac{2m}{l}(x^2 + y^2 + z^2) = \frac{2mu^2}{l}.$$

There being n molecules, the total effect will be $\frac{2\ mnu^2}{l}$. The entire inner surface of the cubical vessel being $6l^2$, the pressure p, on unit area, will be

$$p = \frac{2mnu^2}{6l^3} = \frac{1}{3} \cdot \frac{mnu^2}{l^3}.$$

But since l^3 is the volume of the cube, which we will denote by v, we have

$$p = \frac{1}{3} \cdot \frac{mnu^2}{v},$$

or

$$pv = \frac{1}{3} \cdot mnu^2. \tag{5}$$

This is the fundamental equation of the kinetic theory of gases. While the equation has been derived for a cubical vessel, it is equally applicable to a vessel of any shape whatever, since the total volume may be considered to be made up of a large number of infinitesimally small cubes, for each of which the equation holds.

Deductions from the Kinetic Equation. *Law of Boyle.* In the fundamental kinetic equation, $pv = \frac{1}{3}\ mnu^2$, the right-hand side is composed of factors which are constant at constant temperature, and therefore the product, pv, must be constant also under similar conditions. This is clearly Boyle's law.

Law of Gay-Lussac. The kinetic equation may be written in the form,

$$pv = \frac{2}{3} \cdot \frac{1}{2} mnu^2. \tag{6}$$

The kinetic energy of a single molecule being represented by $1/2\ mu^2$, the total kinetic energy of the molecules of the gas will be $1/2\ mnu^2$. *Therefore the product of the pressure and volume of the gas is equal to two-thirds of the total kinetic energy of its molecules.* Since the mean kinetic energies of all gases are identical at the same temperature, it follows that any change in the kinetic energy resulting from a change in temperature must be directly proportional to the latter, otherwise the mean kinetic energies of the gas molecules which were equal at one temperature could not be so at any other. But equation (6) teaches that the product of the pressure and volume of a gas is directly proportional to the total kinetic energy of its molecules, and a change in temperature must therefore alter this product to the same extent for each gas. If the pressure be maintained constant, the volume alone will undergo change, or vice versa, if the volume remains constant the pressure only will be altered. In either case, whichever factor of the product, pv, undergoes change, the kinetic theory shows that the rate

of this change with temperature is the same for all gases. This, it will be observed is a statement of the law of Gay-Lussac.

Hypothesis of Avogadro. If equal volumes of two different gases are measured under the same pressure, we will have

$$pv = 1/3\, n_1 m_1 u_1^2 = 1/3\, n_2 m_2 u_2^2, \tag{7}$$

where n_1 and n_2, m_1 and m_2, and u_1 and u_2 denote the number, mass and velocity of the molecules in the two gases. If the gases are measured at the same temperature, the molecules of each possess the same mean kinetic energy, or

$$1/2\, m_1 u_1^2 = 1/2\, m_2 u_2^2. \tag{8}$$

Dividing equation (7) by equation (8), we have

$$n_1 = n_2,$$

or under the same conditions of temperature and pressure equal volumes of the two gases contain the same number of molecules. This is the hypothesis of Avogadro.

Law of Graham. If the fundamental kinetic equation be solved for u, we have

$$u = \sqrt{\frac{3\,pv}{mn}};$$

but $v/mn = 1/d$, where d is the density of the gas, and therefore we may write

$$u = \sqrt{\frac{3\,p}{d}}. \tag{9}$$

If the pressure and temperature remain constant, it is evident that the mean velocities of the molecules of two gases are inversely proportional to the square roots of their densities, a law which was first enunciated by Graham as the result of his experiments on gaseous effusion.

Effusion of Gases. Let u_1 and u_2 denote the mean velocities of translation of the molecules of any two gases whose densities are d_1 and d_2 respectively. Then, if both pressure and temperature are constant, we may write, according to equation (9),

$$\frac{u_1}{u_2} = \sqrt{\frac{d_2}{d_1}};$$

or, letting M_1 and M_2 denote the molecular weights of the two gases, we have

$$\frac{u_1}{u_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \tag{10}$$

The tendency of gases to effuse through small apertures is a manifestation of the motion of their molecules, and it was from experiments on the rate of such gaseous effusion that Graham was led to the discovery of the law which bears his name.

By observing the times of effusion, at constant temperature, of equal volumes of two different gases through the same aperture, and under the same difference of pressure, it is possible to determine the density of one gas, provided that of the other is known. Since the times of effusion, t_1 and t_2, are inversely proportional to the velocities, u_1 and u_2, equation (10) becomes

$$\frac{t_1}{t_2} = \sqrt{\frac{d_1}{d_2}} = \sqrt{\frac{M_1}{M_2}}. \tag{11}$$

This method of determining the density and molecular weight of gases was developed by Bunsen, and has proved to be of great value, especially in cases where only a small volume of gas is available. Thus, Debierne* applied the method of effusion to the determination of the molecular weight of the radium emanation and, notwithstanding the very small volume of gas obtainable, he found the value of the molecular weight to be 220 which is in remarkably close agreement with 222, the accepted value.

Mean Velocity of Translation of a Gaseous Molecule. By substituting appropriate values for the various magnitudes in the equation

$$u = \sqrt{\frac{3\,pv}{mn}},$$

it is possible to calculate the mean velocity of the molecules of any gas. Thus, for the gram-molecule of hydrogen at 0° and 76 cm. pressure, $p = 76 \times 13.59 = 1033.3$ gr. per sq. cm. $= 1033.3 \times 980.6$ dynes per sq. cm., $v = 22{,}400$ cc., and $mn = 2.016$ gr.

Substituting these values in the above equation we have,

$$u = \sqrt{\frac{3 \times 1033.3 \times 980.6 \times 22{,}400}{2.016}} = 183{,}780 \text{ cm. per sec.}$$

* Compt. rend. 150, 1740 (1910).

Thus at 0° the molecule of hydrogen moves with a speed slightly greater than one mile per second. This enormous speed is only attained along the mean free path, the frequent collisions with other molecules rendering the actual speed much less than that calculated.

Equation of van der Waals. As has been pointed out in a previous paragraph, the gas laws are merely limiting laws and while they hold quite well up to pressures of about 2 atmospheres, above this pressure the differences between the observed and calculated values become steadily larger. In the case of hydrogen, Natterer was the first to show that the product of pressure and volume is invariably higher than it should be. A possible explanation of this departure from the gas laws was offered by Budde, who proposed that the volume, v, in the equation $pv = RT$, should be corrected for the volume occupied by the molecules themselves. If this volume correction be denoted by b, then the gas equation becomes

$$p\,(v - b) = RT, \tag{12}$$

where b is a constant for each gas. Budde calculated the value of b for hydrogen and found it to remain constant for pressures varying from 1000 to 2800 meters of mercury.

While Budde's modification of the gas equation is quite satisfactory in the case of hydrogen, it fails when applied to other gases. In general, the compressibility at low pressures is considerably greater than can be accounted for by Boyle's law. The compressibility reaches a minimum value, and then increases rapidly, so that pv passes through the value required by the law. This suggests that there is some other correction to be applied in addition to the volume correction introduced into the gas equation by Budde. In 1879, van der Waals pointed out that in the deduction of Boyle's law by means of the fundamental kinetic equation, the tacit assumption is made that the molecules exert no mutual attraction. While this assumption is undoubtedly justifiable when the gas is subjected to a very low pressure, it no longer remains so when the gas is strongly compressed. A little consideration will make it apparent that when increased pressure is applied to a gas, the resulting volume will become less than that calculated, owing to molecular attraction. In other words the molecular attraction and the applied pressure act in the same direction and the gas

behaves as if it were subjected to a pressure greater than that actually applied. It was shown by van der Waals that this correction is inversely proportional to the square of the volume, and since it augments the applied pressure, the expression, $p + a/v^2$, should be substituted for p in the gas equation, a being the constant of molecular attraction. The corrected equation then becomes

$$(p + a/v^2)\,(v - b) = RT. \qquad (13)$$

This is known as the equation of van der Waals. It is applicable not only to strongly compressed gases, but also to liquids as well. While it will be given detailed consideration in a subsequent chapter, it may be of interest to point out at this time, the satisfactory explanation which it offers of the experimental results of Amagat, to which we have already made reference (page 24). When v is large, both b and a/v^2 become negligible, and van der Waals' equation reduces to the simple gas equation, $pv = RT$. We may predict, therefore, that any influence tending to increase v will cause the gas to approach more nearly to the ideal condition. This is in accord with the results of Amagat's experiments, which show that an increase of temperature at constant pressure, or a diminution of pressure at constant temperature, causes the gas to tend to follow the simple gas laws. The equation also offers a satisfactory explanation of the exceptional behavior of hydrogen when it is subjected to pressure. As we have seen, pv for all gases, except hydrogen, diminishes at first with increasing pressure, reaches a minimum value, and then increases regularly. Since the volume correction in van der Waals' equation acts in opposition to the attraction correction, it is apparent that at low pressures the effect of attraction preponderates, while at high pressures the volume correction is relatively of more importance. At some intermediate pressure the two corrections counterbalance each other, and it is at this point that the gas follows Boyle's law strictly. The exceptional behavior of hydrogen may be accounted for by making the very plausible assumption that the attraction correction is negligible at all pressures in comparison with the volume correction.

Vapor Density and Molecular Weight. The ratio of the weight of a definite volume of vapor or gas to that of an equal volume of hydrogen measured at the same temperature and pressure is known as its *vapor density*. Numerically vapor densities and molecular weights are identical. As has been pointed out in an

earlier chapter, when a substance can be obtained in the gaseous state, the determination of its molecular weight resolves itself into finding the mass of that volume of vapor which will occupy 22.4 liters at 0° and 76 cm. It is inconvenient to weigh a volume of gas or vapor under standard conditions of temperature and pressure, but by means of the gas laws the determination made at any temperature and under any pressure can be reduced to standard conditions. For example, suppose v cc. of gas are found to weigh w grams at $t°$ and p cm. pressure, then the weight in grams of 22.4 liters or 22,400 cc. at 0° and 76 cm. will be given by the following proportion, in which M denotes the molecular weight of the substance: —

$$w : \frac{pv}{t + 273} = M : \frac{76 \times 22{,}400}{273},$$

or

$$M = \frac{w \times 76 \times 22{,}400 \times (t + 273)}{273\ pv}.$$

The determination of vapor density may be effected in either of two ways; (1) we may determine the mass of a known volume of vapor under definite conditions of temperature and pressure, or (2) we may determine the volume of a known mass under definite conditions of temperature and pressure. There are a variety of methods for the determination of vapor density; but for our purpose it will be necessary to describe but two of them. In the method of Regnault the mass of a definite volume of vapor is determined, while in the method due to Victor Meyer we measure the volume of a known mass.

Method of Regnault. In this method which is especially adapted to permanent gases, use is made of two spherical glass bulbs of approximately the same capacity, each bulb being provided with a well-ground stop-cock. By means of an air pump one bulb is evacuated as completely as possible, and is then filled, at definite temperature and pressure, with the gas whose density is to be determined. The stop-cock is then closed and the bulb weighed, the second bulb being used as a counterpoise. The use of the second bulb is largely to avoid the troublesome corrections for air displacement and for moisture, each bulb being affected in the same way and to nearly the same extent. The volume of the bulb may be obtained by weighing it first evacuated, and then filled with distilled water at known temperature. From these results we may calculate the mass per unit of volume; or we may

substitute the values of w, v, p and t in the above formula and calculate M, the molecular weight. This method was used by Morley* in his epoch-making research on the densities of hydrogen and oxygen.

Method of Victor Meyer. In the method of Victor Meyer, a weighed amount of the substance is vaporized, and the volume

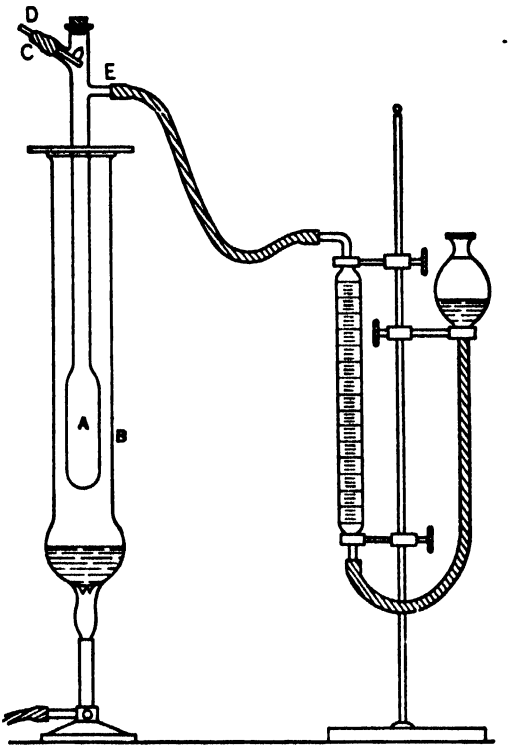

Fig. 7

which it would have occupied at the temperature of the room and under existing barometric pressure is determined. The apparatus of Meyer, shown in Fig. 7, consists of an inner glass tube A, about 1 cm. in diameter and 75 cm. in length. This tube is expanded into a bulb at the lower end, while at the top it is slightly enlarged and is furnished with two side tubes C and E. The tube A is suspended inside a heating jacket B, containing some liquid the boiling point of which is about 30° higher than the vaporizing

* Smithsonian Contributions to Knowledge (1895).

temperature of the substance whose vapor density is to be determined. The side tube, E, leads to a burette furnished with a leveling tube and filled full of water or mercury. A small bulb containing a known weight of the substance whose vapor density is sought is inserted in the upper part of the tube, A, and is prevented from falling by means of a glass rod, D, projecting through the side tube, C. The joint between D and C is made with rubber tubing so that the glass rod may be pulled outward and the bulb permitted to drop to the bottom of A.

To carry out a determination of vapor density with this apparatus, the liquid in B is heated until it boils and the sealed bulb, containing a weighed amount of the substance, is placed in position on the rod, D, and the cork tightly inserted. The level of the liquid in the burette is now noted. When the temperature in A has become constant, there will be no further change in the level of the liquid in the burette. Having assured oneself that the temperature in A is constant, the rod D is pulled out, and the bulb is allowed to drop to the bottom of A. The impact together with the increase in temperature causes the bulb to break and the substance vaporizes at the bottom of A, driving out an equal volume of air which is collected in the burette. The position of the leveling bulb is now adjusted and the volume of the displaced air in the burette is measured. It is evident that in this method we do not require a knowledge of the temperature at which the substance vaporizes. Since the air is measured over water, the pressure to which it is subjected is that of the atmosphere diminished by the vapor pressure of water at the temperature of the experiment.

The method of calculating molecular weights from the observations recorded may be illustrated by the following example: — 0.1 gram of benzene (C_6H_6) was weighed out, and when vaporized, 32 cc. of air were collected over water at 17° and 750 mm. pressure. The vapor pressure of water at 17° is 14.4 mm., and the actual pressure exerted by the gas is 750 − 14.4 = 735.6 mm. Substituting in the proportion

$$w : \frac{pv}{t + 273} = M : \frac{760 \times 22{,}400}{273},$$

and solving for M we have

$$M = \frac{0.1 \times 760 \times 22{,}400 \times (17 + 273)}{273 \times 735.6 \times 32} = 76.8.$$

The result agrees fairly well with the molecular weight of benzene (78.05) calculated from the formula.

An improved form of the Victor Meyer apparatus, devised by Lumsden,* is shown in Fig. 8. It consists of a bulb, *A*, surrounded by a heating jacket, *B*, and a manometer *C*. A weighed amount of substance is dropped into the bulb and vaporized and

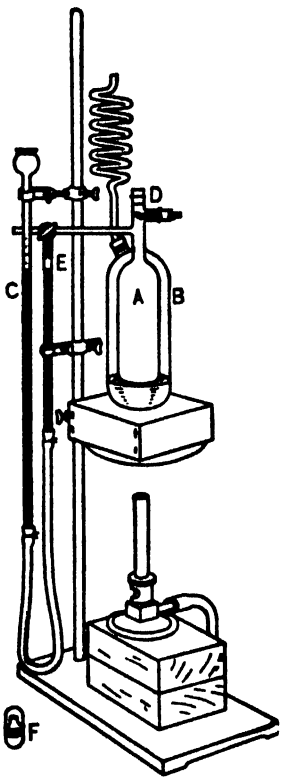

Fig. 8

the pressure measured before diffusion takes place. The bulb has a capacity of approximately 100 cc., and the inlet-tube, *D*, having a diameter of about 8 mm., has a side tube for the insertion of glass rod to support the substance before it is dropped into the bulb. A tube of small bore, furnished with a three-way tap, connects with the manometer. Just below this tap a piece of wider

* Jour. Chem. Soc. 83, 342 (1903).

tubing of the same calibre as the measuring tube of the manometer is attached. A mark, E, is made on the fixed arm of the manometer so that when the mercury is raised to that height, the same volume of gas will always be enclosed.

In order to carry out a determination of vapor density with this apparatus, the liquid in the outer jacket is boiled for at least fifteen minutes to insure that the whole apparatus has been heated and that the temperature is constant. The temperature inside of the bulb should then be that of the boiling point of the heating liquid. The tap being open to the air, the mercury is levelled to the mark, and the substance, sealed in a small bulb, is placed on its support. The rubber stopper is then inserted, the tap closed to the air, and the tiny bulb allowed to fall into the vaporizing chamber. While the substance is being vaporized, the graduated measuring tube is raised in order to keep the level of the mercury near the mark. As soon as the pressure becomes constant, the manometer tubes are placed close together, the mercury carefully adjusted to the mark, and the difference in level in the two tubes carefully measured. This reading corresponds to the pressure due to the vapor of the substance.

When used as an instrument to give absolute measurements, the capacity of the apparatus must obviously be known. This may be readily found by filling the bulb and tubes with water from a burette, or by finding the weight of water necessary to fill the apparatus. Having determined the capacity of the apparatus and knowing the temperature and the pressure due to the vapor of the substance, its molecular weight may be deduced as follows: — Let V be the capacity of the apparatus, P the barometric pressure, and p the increase in pressure due to the vapor of the substance. Since volume V becomes, with the added vapor, $V(P + p)/P$, the volume of the vapor is $V(P + p)/P - V = Vp/P$. This volume at P and $t°$ becomes, at 760 mm. and 0°, $Vp \cdot 273/760\ (t + 273)$. The weight w of substance producing this volume of vapor being known, and assuming that a gram-molecular weight of the substance will occupy 22.4 liters at 0° and 760 mm., the molecular weight, M, of the substance will be given by the expression,

$$M = \frac{22.4\ (t + 273)\ 760}{273\ V} \cdot \frac{w}{p}.$$

Unless a vapor follows the gas laws very closely, the value of the molecular weight obtained by the method of Victor Meyer will be only approximate, but this approximate value will be sufficiently near to the true molecular weight to enable us to choose between the simple formula weight, given by chemical analysis, and some multiple of it.

Results of Vapor-Density Determinations. As the result of numerous vapor-density determinations extending over a wide range of temperatures, much important information has been collected concerning the number of atoms contained in the molecules of a large number of chemical compounds. The molecular weights of most of the elementary gases are double their atomic weights, showing that their molecules are diatomic. In like manner the molecular weights of mercury, zinc, cadmium and, in fact, all of the vaporizable metallic elements have been found to be identical with their atomic weights. The molecules of sulphur, arsenic, phosphorus and iodine are polyatomic, if they are not heated to too high a temperature. The investigations of Meyer and others have shown that the vapor densities of a large number of substances diminish as the temperature is increased. In other words as the temperature is raised the number of atoms contained in the molecules decreases. The molecular weight of sulphur, calculated from its vapor density at temperatures below 500°, corresponds to the formula S_8. If the vapor of sulphur is heated to 1100°, the molecular weight corresponds to the formula S_2. In fact, sulphur in the form of vapor may be represented by the formulas S_8, S_4, S_2, or even S according to the temperature at which its vapor density is determined. Iodine behaves similarly, the molecules being diatomic between 200° and 600°, while at temperatures above 1400° the vapor density has about one-half its value at the lower temperature, showing a complete breaking down of the diatomic molecules into single atoms. Heating to yet higher temperatures has failed to reveal any further decomposition. This phenomenon is not confined to the molecules of the elements alone, but is also met with in the case of the molecules of chemical compounds. The vapor density of arsenious oxide between 500° and 700° corresponds to the formula As_4O_6. As the temperature is raised, the vapor density becomes steadily smaller until, at

1800°, the calculated molecular weight corresponds to the formula As_2O_3. In like manner ferric and aluminium chlorides have been shown to have molecular weights at low temperatures corresponding to the formulas, Fe_2Cl_6 and Al_2Cl_6. The commonly-used formulas, $FeCl_3$ and $AlCl_3$, represent their molecular weights at high temperatures only. The experimental difficulties attending vapor density determinations increase as the temperature is raised, owing chiefly to the deformation of the apparatus when the material of which it is constructed approaches its melting-point. Glass which can be used at relatively low temperatures only, has been replaced by specially resistant varieties of porcelain which may be used up to temperatures of 1500° or 1600°. Platinum vessels retain their shape up to temperatures between 1600° and 1700°. Measurements up to 2000° have been effected by Nernst and his pupils.* In their experiments use was made of a vessel of iridium, the inside and outside of which was surrounded with a cement of magnesia and magnesium chloride, the entire apparatus being heated electrically. With this apparatus they showed that the molecular weight of sulphur between 1800° and 2000° is 48, indicating that the diatomic molecule is approximately 50 per cent broken down into single atoms.

Abnormal Vapor Densities. In all of the cases cited above the molecular weight calculated from the vapor density corresponds either with the simple formula weight, as determined by chemical analysis, or with a multiple thereof. In no case is there any evidence of a breaking down of the simple molecule into its constituents. Substances are known, however, the molecular weights of which, calculated from their vapor densities, are less than the sum of the atomic weights of their constituents. For example, the vapor density of ammonium chloride was found to be 0.89, while that corresponding to the formula NH_4Cl should be 1.89. Similar results have been obtained with phosphorus pentachloride, nitrogen peroxide, chloral hydrate and numerous other substances. The phenomenon can be explained in either of the two following ways: (1) that the molecule has undergone a complete disruption, or (2) that the substance does not follow the law of Avogadro. Until the former explanation was shown to be correct, the latter was accepted and for a time the law of Avogadro

* Wartenberg. Zeit. anorg. Chem., 56, 320 (1907).

fell into disrepute. In 1857, Deville showed that numerous chemical compounds are broken down or " dissociated " at high temperatures. Shortly afterward Kopp suggested that the abnormal vapor densities of such substances as ammonium chloride, phosphorus pentachloride, etc., might be due to thermal dissociation. If ammonium chloride underwent complete dissociation, one molecule of the salt would yield one molecule of ammonia and one molecule of hydrochloric acid gas, and the vapor density of the resulting mixture would be one-half of that of the undissociated substance, a deduction in complete agreement with the results of experiment. It remained to prove that the products of this supposed dissociation were actually present.

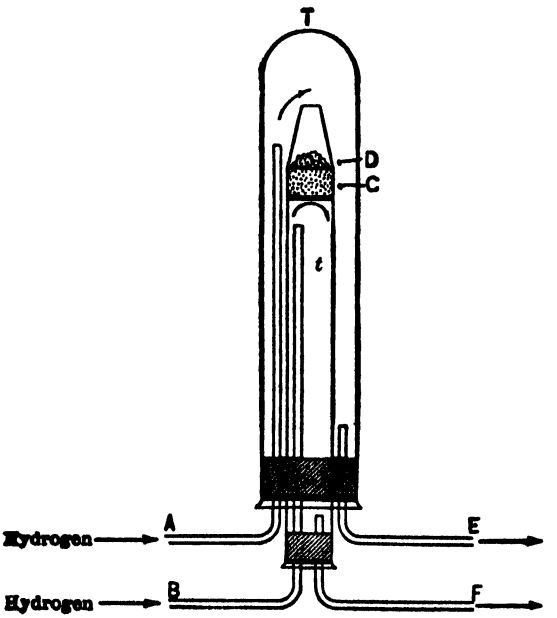

Fig. 9

The first to offer an experimental demonstration of the simultaneous formation of ammonia and hydrochloric acid, when ammonium chloride is heated, was Pebal.* The apparatus which he devised for this purpose is shown in Fig. 9. It consisted of two tubes *T* and *t*, the latter being placed within the former as indi-

* Lieb. Ann., 123, 199 (1862).

cated in the sketch. Near the top of the inner tube, which was drawn down to a smaller diameter, was a porous plug of asbestos, *C*, upon which was placed a little ammonium chloride. A stream of dry hydrogen was passed through the apparatus by means of the tubes *A* and *B*, the former entering the outer tube and the latter the inner tube. The entire apparatus was heated to a temperature above that necessary to vaporize the ammonium chloride. If the salt undergoes dissociation into ammonia and hydrochloric acid, the former being less dense than the latter, would diffuse more rapidly through the plug *C* and the vapor below the plug would be relatively richer in ammonia than the vapor above it. The current of hydrogen through *B* would therefore sweep out from the lower part of *t* an excess of ammonia, while the current through *A* would carry out from *T* an excess of hydrochloric

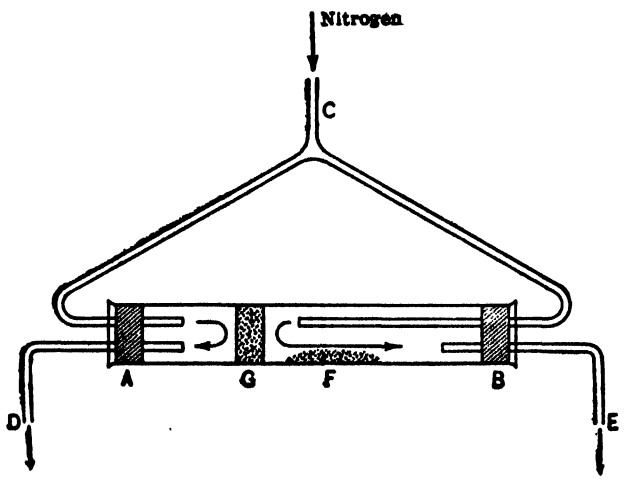

Fig. 10

acid. By holding strips of moistened litmus paper in the currents of gas issuing from *E* and *F*, it was possible for Pebal to test the correctness of Kopp's idea. He found that the gas issuing from *E* had an acid reaction while that escaping from *F* had an alkaline reaction. It would at first sight appear that Pebal had demonstrated beyond question that ammonium chloride undergoes dissociation into ammonia and hydrochloric acid.

It was pointed out, however, that Pebal had heated the ammonium chloride in contact with a foreign substance, asbestos, and

that this might have acted as a catalyst, promoting the decomposition into ammonia and hydrochloric acid. This objection was removed by the ingenious experiment of Than.* He devised a modification of Pebal's apparatus, as shown in Fig. 10. In the horizontal tube, AB, the ammonium chloride was placed at F and a porous plug of compressed ammonium chloride was introduced at G. The tube was heated and nitrogen passed in at C. The reactions of the currents of gas issuing at D and E were tested with litmus, as in Pebal's experiment, and it was found that the gas escaping from D was alkaline, while that issuing from E was acid. This experiment proved beyond question that the vapor of ammonium chloride is thermally dissociated into ammonia and hydrochloric acid. Experiments on other substances whose vapor densities are abnormally small show that a similar explanation is applicable, and thus furnish a confirmation of the law of Avogadro.

Calculation of the Degree of Dissociation. Since the density of a dissociating vapor decreases with increase in temperature, it is important to be able to calculate the degree of dissociation at any one temperature. This is clearly equivalent to ascertaining the extent to which the reaction

$$NH_4Cl \rightleftarrows NH_3 + HCl$$

has proceeded from left to right. This can be determined easily from the relation of vapor density to dissociation. If we start with one molecule of gas and let α represent the percentage dissociation, then $1 - \alpha$ will denote the percentage remaining undissociated. If one molecule of gas yields n molecules of gaseous products, the total number of molecules present at any time will be

$$(1 - \alpha) + n\alpha = 1 + (n - 1)\alpha.$$

The ratio, $1 : 1 + (n - 1)\alpha$, will be the same as the ratio of the density d_2 of the dissociated gas to its density in the undissociated state d_1, or

$$1 : 1 + (n - 1)\alpha = d_2 : d_1;$$

solving this proportion for α, we have

$$\alpha = \frac{d_1 - d_2}{(n - 1)\, d_2}. \qquad (14)$$

* Lieb. Ann., 131, 129 (1864).

The vapor density of nitrogen peroxide has been measured by E. and L. Natanson,* and the degree of dissociation at the different temperatures calculated by means of the preceding formula. The following table gives their results.

DISSOCIATION OF NITROGEN PEROXIDE, N_2O_4

ATMOSPHERIC PRESSURE

Temperature. (degrees)	Vapor Density	Per cent of N_2O_4 molecules dissociated
26.7	38.3	20.1
35.4	36.5	26.0
39.8	35.5	29.6
49.6	32.8	40.3
60.2	30.0	53.3
70.0	27.7	66.0
80.6	26.0	77.0
90.0	24.8	85.4
100.1	24.3	89.5
111.3	23.8	93.2
121.5	23.4	96.6
135.0	23.1	99.2
154.0	23.0	100.0

It will be observed that the dissociation of nitrogen peroxide is, at first nearly proportional to the temperature, and then increases more rapidly until, when about four-fifths of the molecules of N_2O_4 are broken down, the dissociation proceeds slowly to completion.

Specific Heat. The addition of heat energy to a body causes its temperature to rise. The ratio of the amount of heat supplied to the resulting rise in temperature is called the *heat capacity* of the body; obviously its value is dependent upon the initial temperature of the body. The *specific heat* of a substance may be defined as *the heat capacity of unit mass of the substance.* If dt represents the increment of temperature due to the addition of dQ units of heat energy to m grams of any substance, then its specific heat, c, will be given by the equation

$$c = \frac{1}{m} \cdot \frac{dQ}{dt}. \tag{15}$$

* Wied. Ann., 24, 454 (1885); 27, 606 (1886).

Specific Heat at Constant Pressure and Constant Volume. It is well known that the specific heat of a gas depends upon the conditions under which it is determined. If a definite mass of gas is heated under constant pressure, the value of the specific heat, c_p, is different from the value of the specific heat, c_v, obtained when the pressure varies and the volume remains constant. The value of c_p is invariably greater than that of c_v. When heat is supplied to a gas at constant pressure not only does its temperature rise, but it also expands, and thus does external work. On the other hand, if the gas be heated in such a way that its volume cannot change, none of the heat supplied will be used in doing external work, and consequently its heat capacity will be less than when it is heated under constant pressure. The recognition by Mayer, in 1841, of the cause of this difference between the two specific heats of a gas, led him to his celebrated calculation of the mechanical equivalent of heat, and the enunciation of the first law of thermodynamics. Mayer observed that the difference between the quantity of heat necessary to raise the temperature of 1 gram of air 1° C. at constant pressure, and at constant volume respectively, was 0.0692 calorie, or

$$c_p - c_v = 0.0692 \text{ cal.}$$

That is to say, 0.0692 calorie is the amount of heat energy which is equivalent to the work required to expand 1 gram of air 1/273 of its volume at 0°. Imagine 1 gram of air at 0° enclosed within a cylinder having a cross-section of one square centimeter, and furnished with a movable, frictionless piston. Since 1 gram of air under standard conditions of temperature and pressure occupies 773.3 cc., the distance between the piston and the bottom of the cylinder will be 773.3 cm. If the temperature be raised from 0° to 1°, the piston will rise $1/273 \times 773.3 = 2.83$ cm., and since the pressure of the atmosphere is 1033.3 grams per square centimeter, the external work done by the expanding gas will be

$$1033.3 \times 2.83 = 2924.3 \text{ gm. cm.}$$

This is evidently equivalent to 0.0692 calorie and therefore, the equivalent of 1 calorie in mechanical units, J, will be

$$J = \frac{2924.3}{0.0692} = 42{,}258 \text{ gm. cm.},$$

a value agreeing very well with the best recent determinations of the mechanical equivalent of heat.

The difference between the two specific heats may be easily calculated in calories from the fundamental gas equation. Starting with 1 mol of gas, and remembering that when a gas expands at constant pressure, the product of pressure and change in volume is a measure of the work done, we have, at temperature T_1,

$$pv_1 = RT_1,$$

where v_1 is the molecular volume. Raising the temperature to T_2, the corresponding molecular volume being v_2, we have for the work done during expansion

$$p(v_2 - v_1) = R(T_2 - T_1).$$

If $T_2 - T_1 = 1°$, then the equation reduces to

$$p(v_2 - v_1) = R.$$

Since the difference between the molar heats* at constant pressure and constant volume is equivalent to the external work involved when the temperature of 1 mol of gas is raised 1°, we have

$$M\,(c_p - c_v) = p\,(v_2 - v_1),$$

where M is the molecular weight of the gas; and therefore,

$$M\,(c_p - c_v) = R = 2 \text{ calories.} \qquad (16)$$

In words, the difference of the molar heats of any gas at constant pressure and at constant volume is 2 calories. The specific heat of a gas at constant pressure can be readily determined, by passing a definite volume of the gas, heated under constant pressure to a known temperature, through the worm of a calorimeter at such a rate that a constant difference is maintained between the temperature of the entering and the temperature of the escaping gas. Thus the number of calories which cause a definite thermal change in a certain volume of the gas is determined, and from this it is an easy matter to calculate the specific heat, c_p.

* *The molar heat of a gas is equal to the product of its specific heat and its molecular weight.*

The molecular heat at constant pressure for all gases approaches the limiting value, 6.5, at the absolute zero. This relation, due to Le Chatelier, may be expressed thus,

$$Mc_p = 6.5 + aT, \tag{17}$$

where a is a constant for each gas. The value of a for hydrogen, oxygen, nitrogen and carbon monoxide is 0.001, for ammonia, 0.0071 and for carbon dioxide, 0.0084. As the complexity of the gas increases the value of a becomes numerically greater.

The experimental determination of the specific heat of a gas at constant volume is difficult and the results obtained are not trustworthy. The chief cause of the inaccuracy of the results is that the vessel containing the gas absorbs so much more heat than the gas itself that the correction is many times larger than the quantity to be measured. The specific heat at constant volume is almost always obtained by indirect methods, as for example by means of the preceding formula,

$$M\,(c_p - c_v) = R = 2 \text{ cal.},$$

in wnich the values of M and c_p are known.

The molecular heats of some of the commoner gases and vapors are given in the subjoined table together with the ratio c_p/c_v.

MOLAR HEAT CAPACITIES

Gas.	Mc_p	Mc_v	$c_p/c_v=\gamma$
Argon	.....	.....	1.66
Helium	.....	.....	1.66
Mercury	.....	.....	1.66
Hydrogen	6.88	4.88	1.41
Oxygen	6.96	4.96	1.40
Nitrogen	6.93	4.93	1.41
Chlorine	8.58	6.58	1.30
Bromine	8.88	6.88	1.29
Nitric oxide	6.95	4.95	1.40
Carbon monoxide	6.86	4.86	1.41
Hydrochloric acid	6.68	4.68	1.43
Carbon dioxide	9.55	7.55	1.26
Nitrous oxide	9.94	7.94	1.25
Water	8.65	6.65	1.28
Sulphur dioxide	9.88	7.88	1.25
Ozone	.....	.....	1.29
Ether	35.51	33.51	1.06

The Ratio of the Two Specific Heats. There are two methods by which the ratio c_p/c_v can be determined directly, one due to Clement and Desormes* and the other due to Kundt.†

Method of Clement and Desormes. The gas to be investigated is introduced into a large glass balloon under a pressure P_1 which is only a trifle greater than atmospheric pressure, P. The flask is now opened for a moment in order to allow the pressure within the vessel to fall to that of the atmosphere, after which it is again closed. The expansion of the gas, resulting from the momentary opening of the flask, causes a slight lowering of its temperature. Thermal equilibrium is again restored by the influx of heat from without, which in turn, causes the pressure in the vessel to increase to a value P_2 slightly greater than atmospheric pressure. Let $P_1 = P + p_1$ and $P_2 = P + p_2$, where p_1 and p_2 are small in comparison with P. If V denotes the volume of the flask, the volume of gas which escapes when the flask is opened is $V(p_1 - p_2)/P$, and the work done against the atmosphere is $V(p_1 - p_2)$. This is the amount of work resulting from the expansion of the gas, which is assumed to take place so rapidly that the system neither gains nor loses heat. The pressure of the gas increases from P to $P + p_2$ in consequence of the restoration of thermal equilibrium following the closing of the flask, and the value of t, the number of degrees by which the gas is cooled below the temperature of the room, T, can be calculated by means of the proportion,

$$t/T = p_2/P.$$

Since the influx of heat occurs at constant volume, and as the number of gram-molecules of gas contained in the flask is

$$n = PV/RT,$$

it follows that the number of calories taken up by the gas must be

$$\frac{PV}{RT} Mc_v t = \frac{p_2 V}{R} Mc_v.$$

This quantity of heat is equivalent to $V(p_1 - p_2)$, the work performed by the gas. Therefore, we have

$$V(p_1 - p_2) = \frac{p_2 V}{R} Mc_v,$$

* Jour. de phys., 89, 321, 428 (1819).

† Pogg. Ann., 128, 497 (1866); 135, 337, 527 (1868).

or

$$p_1 - p_2 = \frac{p_2}{R} M c_v.$$

But, according to eq. (16),

$$R = M\,(c_p - c_v).$$

Hence

$$\frac{p_1}{p_1 - p_2} = \frac{c_p}{c_v} = \gamma. \qquad (18)$$

Owing to the fact that some heat is removed from the walls of the flask during the escape of the undercooled gas, the observed value t, and the corresponding value of p_2, will be too small, and therefore the calculated value of γ will likewise be too small. This source of error can be minimized by using a large flask and making the differences of pressure as small as possible.

Method of Kundt. According to the formula of Laplace for the velocity of transmission of a sound wave in a gas, we have

$$v = \sqrt{\gamma \frac{p}{d}},$$

in which p and d denote the pressure and density of the gas, and γ is the ratio of the two specific heats. If the wave velocities in two different gases, whose densities are d_1 and d_2 under the same conditions of temperature and pressure, be denoted by v_1 and v_2, we may write

$$\frac{v_1}{v_2} = \sqrt{\frac{\gamma_1 d_2}{\gamma_2 d_1}},$$

or replacing the densities of these gases by their respective molecular weights, M_1 and M_2, we have

$$\frac{v_1}{v_2} = \sqrt{\frac{\gamma_1 M_2}{\gamma_2 M_1}}. \qquad (19)$$

The ratio of the velocities of the two waves can be measured by means of the apparatus shown in Fig. 11. A wide glass tube about 1½ meters in length is furnished with two side tubes, E and F. Into one end of the tube is inserted the glass rod BD which is clamped at its middle point by a tightly fitting cork, C. The other end of the tube is closed by means of the plunger A. A small amount of lycopodium powder is placed upon the bottom of

the tube and is distributed uniformly by gently tapping the walls of the tube. The gas in which the velocity of the sound wave is to be determined, is introduced into the tube through E, and the displaced air escapes at F. When the tube is filled, E and F are closed by means of rubber caps, and a piece of moistened chamois leather is drawn along BD causing it to vibrate longitudi-

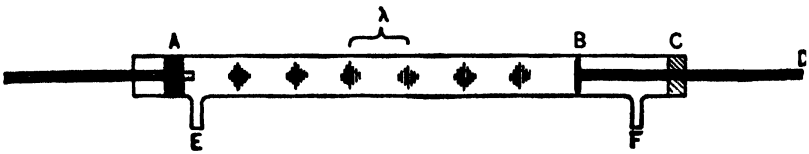

Fig. 11

nally and to emit a shrill note. The vibrations are taken up by the gas in the tube and the powder arranges itself in a series of heaps corresponding to the nodes of vibration. If the nodes are not sharply defined, then A should be moved in or out until they become so. If λ_1 is the distance between two heaps or nodes, then $2\lambda_1$ will be the wave length of the note emitted by the rod BD, and if n represents the number of vibrations per second of the note emitted, we have for the velocity of sound in the gas

$$v_1 = 2n\lambda_1.$$

Similarly if a second gas be introduced into the tube we shall have

$$v_2 = 2n\lambda_2.$$

Therefore,

$$\frac{v_1}{v_2} = \frac{\lambda_1}{\lambda_2}. \tag{20}$$

Substituting in equation (19), we have

$$\frac{\lambda_1}{\lambda_2} = \sqrt{\frac{\gamma_1 M_2}{\gamma_2 M_1}},$$

or

$$\gamma_1 = \gamma_2 \frac{\lambda_1^2}{\lambda_2^2} \cdot \frac{M_1}{M_2}. \tag{21}$$

If the second gas is air, as is usually the case, $\gamma_2 = 1.405$ and $M_2 = 28.74$, (mol. wt. of hydrogen ÷ density of hydrogen referred to air, or $2 \div 0.0696 = 28.74$) or equation (21) becomes

$$\gamma_1 = 1.405 \frac{\lambda_1^2}{\lambda_2^2} \cdot \frac{M_1}{28.74}. \tag{22}$$

Thus, γ for any gas can be determined by this method, provided we know its value for another gas of known molecular weight.

Specific Heat of Gases and the Kinetic Theory. In terms of the kinetic theory, the energy of a gas may be considered to be made up of three parts: (1) the translational energy of the molecules, commonly termed their kinetic energy, (2) the intramolecular kinetic energy, and (3) the potential energy due to interatomic attraction within the molecules. When a gas is heated at constant volume, all three of these factors of the total energy of the molecule may be affected. It is fair to assume, however, that when a monatomic gas, such as mercury vapor, is heated, all of the heat energy supplied is used to augment the translational kinetic energy of the molecules. As we have seen, the fundamental kinetic equation,

$$pv = 1/3\, nmu^2,$$

may be written

$$pv = 2/3 \cdot 1/2\, nmu^2,$$

and since $1/2\, nmu^2$ represents the total kinetic energy of the gas, we have

$$pv = 2/3 \text{ kinetic energy of 1 mol,}$$

or

$$\text{kinetic energy of 1 mol} = 3/2\, pv.$$

But $pv = 2\, T$ calories therefore

$$\text{kinetic energy of 1 mol} = 3\, T \text{ cal.}$$

The kinetic energy of a constant volume of any gas at the temperatures T_1 and T_2, is given by the following equations:

$$3/2\, p_1 v = 3\, T_1, \tag{23}$$

and

$$3/2\, p_2 v = 3\, T_2. \tag{24}$$

Subtracting (23) from (24) we obtain

$$3/2\, (p_2 - p_1)\, v = 3\, (T_2 - T_1), \tag{25}$$

and for an increase in temperature of 1°, (25) becomes

$$3/2\, (p_2 - p_1)\, v = 3 \text{ cal.}$$

The molecular kinetic energy of one mol of a monatomic gas at constant volume is thus increased by 3 calories for each degree rise in temperature. As has already been shown,

$$M\,(c_p - c_v) = 2 \text{ cal.},$$

therefore, since $Mc_v = 3$ calories, $Mc_p = 3 + 2 = 5$ calories, and

$$\gamma = \frac{Mc_p}{Mc_v} = \frac{5}{3} = 1.66. \tag{26}$$

This value of γ is in good agreement with the results of the experiments on mercury vapor which is known to be monatomic. The converse of this method has been employed by Ramsay to prove that the rare gases of the atmosphere are monatomic, the value of γ for all of these gases being 1.66. In the case of polyatomic molecules the heat energy supplied is not only used in increasing their translational kinetic energy, but also in the performance of work within the molecule. The value of the internal work is indeterminate, but it is without doubt constant for any one gas. If the internal work be represented by a, then the value of the ratio of the two specific heats will be

$$\gamma = \frac{Mc_p}{Mc_v} = \frac{5 + a}{3 + a} < 1.66 > 1. \tag{27}$$

Reference to the table on p. 47, giving the value of γ for different gases, will show that this deduction from the kinetic theory is in good agreement with the experimental facts. With increasing complexity of the molecule, it is apparent that the amount of heat expended in doing internal work should increase, and therefore the specific heat should increase also. Inspection of the tables confirms this deduction. The specific heat of monatomic gases is independent of the temperature, while the specific heat of polyatomic gases increases as the temperature is lowered. In fact, at very low temperatures the value of γ approaches 1.66 as a limiting value. This is presumably due to a decrease in the value of the term a in equation (27) as the temperature is lowered. These results may justly be regarded as among the greatest triumphs of the kinetic theory of gases.

REFERENCE

The Kinetic Theory of Gases. Meyer. Translated by R. E. Baynes.

PROBLEMS

1. The volume of a quantity of gas is measured when the barometer stands at 72 cm., and is found to be 646 cc.: what would its volume be at normal pressure? *Ans.* 612 cc.

2. At what pressure would the gas in the preceding problem have a volume of 580 cc.? *Ans.* 80.19 cm.

3. A certain quantity of oxygen occupies a volume of 300 cc. at 0°: find its volume at 91°.

4. The weight of a liter of air under standard conditions is 1.293 grams: to what temperature must the air be heated so that it may weigh exactly 1 gram per liter?

5. At what temperature will the volume of a given mass of gas be exactly double what it is at 17°? *Ans.* 307°.

6. On heating a certain quantity of mercuric oxide it is found to give off 380 cc. of oxygen, the temperature being 23° and the barometric height 74 cm.; what would be the volume of the gas under standard conditions?

7. A liter of air weighs 1.293 grams under standard conditions. At what temperature will a liter of air weigh 1 gram, the pressure being 72 cm.? *Ans.* 61.43°.

8. A quantity of air at atmospheric pressure and at a temperature of 7° is compressed until its volume is reduced to one-seventh, the temperature rising 20° during the process: find the pressure at the end of the operation.

9. The weight of a liter of nitrogen under standard conditions is 1.2579 grams. Calculate the specific gas constant, r. *Ans.* 3007 gm. cm.

10. The time of outflow of a gas is 21.4 minutes, the corresponding time for hydrogen is 5.6 minutes. Find the molecular weight of the gas.

11. The times of effusion of equal volumes of air and carbon dioxide are 36.9 sec., and 45.3 sec. respectively: the density of air referred to O = 16 is 14.477. Calculate the molecular weight of carbon dioxide.

12. Calculate the molecular weight of chloroform from the following data: —

Weight of chloroform taken	0.220 gr.
Volume of air collected over water	45.0 cc.
Temperature of air	20°
Barometric pressure	755.0 mm.
Pressure of aqueous vapor at 20°	17.4 mm.

Ans. 121.1.

13. Calculate the molecular weight of ethylene dibromide from the following data obtained with the Lumsden apparatus for vapor density determination: —

Weight of ethylene dibromide	0.1131 gm.
Increase in pressure	15.1 cm.
Temperature of vaporizing chamber	183°
Volume of apparatus	113 cc.

Ans. 187.2.

14. The density of a gas is 0.23 referred to mercury vapor. What is its molecular weight?

15. Phosphorus pentachloride dissociates according to the equation

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

The molecular weight PCl_5 is 208.28. At 182° the density is 73.5 and at 203° it is 62. Find the degree of dissociation at the two temperatures.

Ans. $\alpha_{182°} = 0.417$, $\alpha_{230°} = 0.68$.

16. The specific heat at constant volume for argon is 0.075, and its molecular weight is 40. How many atoms are there in the molecule?

17. What is the specific heat of carbon dioxide at constant volume, its molecular weight being 44 and the temperature 50°?

18. The specific heat for constant pressure of benzene is 0.295: what is the specific heat for constant volume?

CHAPTER III

LIQUIDS

General Characteristics of Liquids. The most marked characteristic of the liquid state is that a given mass of liquid has a definite volume but no definite form. The volume of a liquid is dependent upon temperature and pressure but to a much smaller degree than is the volume of a gas. The formulas in which the volume of a liquid is expressed as a function of temperature and pressure are largely empirical, and contain constants dependent upon the nature of the liquid. This is undoubtedly due to the fact that in the liquid state the molecules are much less mobile than in the gaseous state. The distance between contiguous molecules being much less in liquids than in gases, the mutual attraction is increased while the mobility is correspondingly diminished. That liquids represent a more condensed form of matter than gases is shown by the change in volume which results when a liquid is vaporized: thus, 1 cc. of water at the boiling point when vaporized at the same temperature occupies a volume of about 1700 cc. A liquid contains less energy than a gas, since energy is always required to transform it into the gaseous state. Since gases can be liquefied by increasing the pressure and lowering the temperature, and since liquids can be vaporized by lowering the pressure and increasing the temperature, it is apparent that there is no generic difference between the two states of matter.

Connection Between the Gaseous and Liquid States. If a gas is compressed isothermally, its state may change in either of two ways depending upon the temperature: — (1) The volume at first diminishes more rapidly than the pressure increases, then in the same ratio and lastly more slowly. When the pressure attains a very high value the volume is but slightly altered. This case has already been considered in the preceding chapter. (2) The volume changes more rapidly than the pressure until, when a certain pressure is reached, the gas ceases to be homogeneous, and partial liquefaction results. For a constant temperature, the pressure

at which liquefaction occurs is invariable for a given gas, while the volume steadily diminishes until liquefaction is complete. Only when the whole mass of gas has been liquefied is it possible to increase the pressure and then, owing to the small compressibility of liquids, a large increase in pressure is required to produce a slight diminution in volume. If the temperature is above a certain point, dependent upon the nature of the gas, the phenomena of compression will follow (1); if below this point, the process will follow (2). That a gas may behave in either of the above ways was first clearly recognized by Andrews* in 1869, in connection with his experiments on the liquefaction of carbon dioxide. He found that if carbon dioxide was compressed, keeping the temperature at 0°, the volume changes more rapidly than the pressure, liquefaction resulting when a pressure of 35.4 atmospheres was reached. As the temperature was raised, he found that a higher pressure was required to liquefy the gas, until at temperatures above 30°.92 it was no longer possible to condense the gas to the liquid state. The temperature above which it was no longer possible to liquefy the gas he termed the *critical temperature*. In like manner the pressure required to liquefy the gas at the critical temperature, he termed the *critical pressure*, and the volume occupied by the gas or the liquid under these conditions he called the *critical volume*.

Isothermals of Carbon Dioxide. The results of Andrew's experiments† on the liquefaction of carbon dioxide are shown in Fig. 12, in which the ordinates represent pressures, and the abscissæ the corresponding volumes, at constant temperature. The curves obtained by plotting volumes against pressures at constant temperatures are called *isothermals*. For a gas which follows Boyle's law, the isothermals will be a series of equilateral hyperbolas. This condition is approximately fulfilled by air, for which three isothermals are given in the diagram. At 48° the isothermal for carbon dioxide is nearly hyperbolic, but as the temperature becomes lower, the isothermals deviate more and more from those for an ideal gas. At the critical temperature, 30°.92, the curve is almost horizontal for a short distance, showing that for a very slight change in pressure there is an enormous shrinkage in volume. At still lower temperatures, 21°.1 and 13°.1,

* Trans. Roy. Soc., 159, 583 (1869).

† loc. cit.

the horizontal portions of the curves are much more pronounced, indicating that during liquefaction there is no change in pressure. When liquefaction is complete, the curves rise abruptly, showing that the change in volume is extremely small for a large increase in pressure; in other words the liquefied gas possesses a small coefficient of compressibility. At any point within the parabolic area, indicated by the dotted line ABC, both vapor and liquid are coexistent; at any point outside, only one form of matter, either liquid or vapor, is present. Andrews' experiments show that there is no fundamental difference between a gas and a liquid. It is apparent from the diagram that when carbon dioxide is subjected to great pressures above its critical temperature, it behaves more like a liquid than a gas; in fact it is difficult to determine whether a highly compressed gas above its critical temperature should be classified as a gas or as a liquid.

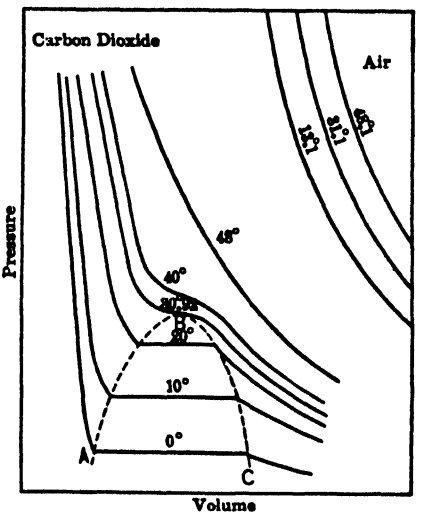

Fig. 12

Van der Waals' Equation and the Continuity of the Gaseous and Liquid States. In the preceding chapter we have learned that the fundamental gas equation,

$$pv = RT,$$

is only strictly applicable to an ideal gas, and that the behavior of actual gases is represented with considerable accuracy, even at high pressures, by the equation of van der Waals,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

If this equation be arranged in descending powers of v, we have

$$v^3 - v^2\left(b + \frac{RT}{p}\right) + v\frac{a}{p} - \frac{ab}{p} = 0. \qquad (1)$$

This being a cubic equation has three possible solutions, each value of p affording three corresponding values of v; a, b, R and T being treated as constants. The three roots of this equation are either all real, or one is real and two are imaginary, depending upon the values of the constants. That is to say, at one temperature and pressure the values of a and b may be such, that v has three real values, while at another temperature and pressure, v may have one real and two imaginary values. In the accompanying diagram, Fig. 13, a series of graphs of the equation for different values of T is given. It will be observed that these curves bear a striking resemblance to the isotherms of carbon dioxide established by the experiments of Andrews. In the case of the theoretical curves there are no sudden breaks such as appear in the actual discontinuous passage from the gaseous to the liquid state. Instead of passing from B to D along the wavelike path BaCbD, experiment has shown that the substance passes directly from the state B to the state D along the straight line BD. It is here that van der Waals' equation fails to apply. As has been pointed out, the substance between these two points is not homogeneous, being partly gaseous and partly liquid. Attempts have been made to realize the portion of the curve BaCbD experimentally. By studying supersaturated vapors and superheated liquids, it has been found possible to follow the theoretical curve for short distances between B and D without discontinuity, but owing to the instability of the substance in this region, it is evident that the complete isothermal and continuous transformation of a gas into a liquid can never be effected. Attention has been called by van der Waals to the fact, that in the surface layer of a liquid, where unique conditions prevail, it is quite possible that such unstable states may exist, and that there the transition from liquid to gas

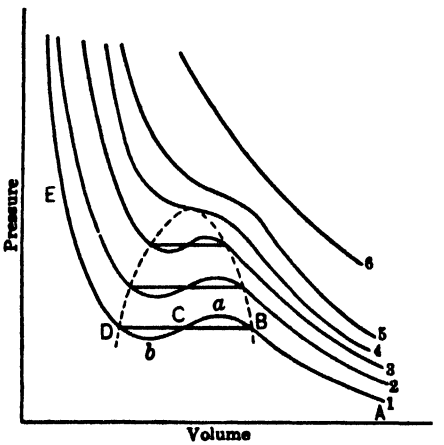

Fig. 13

may in reality be a continuous process. The diagram shows that as T increases, the wavelike portion of the isothermals becomes less pronounced and eventually disappears, when the points B, C and D coalesce. At this point the three roots of the equation become equal, the volume of the liquid becoming identical with the volume of the gas. The substance at this point is in the critical condition. Since under these conditions the three roots of the equation,

$$v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0, \tag{1}$$

are equal, we may write $v_1 = v_2 = v_3 = v_c$, the subscript c indicating the critical state. Then equation (1) must be equivalent to

$$(v - v_c)^3 = v^3 - 3\,v_c v^2 + 3\,v_c^2 v - v_c^3 = 0. \tag{2}$$

Equating the corresponding coefficients of equations (1) and (2), we have

$$3\,v_c = b + \frac{RT_c}{p_c}, \tag{3}$$

$$3\,v_c^2 = \frac{a}{p_c}, \tag{4}$$

and

$$v_c^3 = \frac{ab}{p_c}. \tag{5}$$

Dividing equation (5) by equation (4), we have

$$v_c = 3\,b, \tag{6}$$

and substituting this value in equation (4), we obtain

$$p_c = \frac{a}{27\,b^2}. \tag{7}$$

Lastly, substituting the values of v_c and p_c, given by equations (6) and (7), in equation (3), we have

$$T_c = \frac{8\,a}{27\,bR}. \tag{8}$$

Therefore,

$$\frac{p_c v_c}{T_c} = \frac{3}{8}R. \tag{9}$$

Or expressing the constants a, b and R in terms of the critical values of pressure, temperature and volume, we have

$$a = 3\,p_c v_c^2, \tag{10}$$

$$b = \frac{v_c}{3}, \tag{11}$$

and

$$R = \frac{8\,p_c v_c}{3\,T_c}. \tag{12}$$

By means of equations (6), (7) and (8) it is possible to calculate the critical constants of a gas when the constants a and b of van der Waals' equation are known. Conversely by means of equations (10) and (11), the values of a and b can be calculated when the critical data are given.

The calculated values of the constants, a and b, for several gases are given in the accompanying table. In calculating these values the pressure was measured in atmospheres, and the gram-molecular volume in cubic centimeters. Obviously the value of b must be multiplied by 10^{-3} and that of a by 10^{-6}, if the volume is measured in liters.

VALUES OF VAN DER WAALS' CONSTANTS*

Substance.	Formula.	b.	a.
Hydrogen	H_2	23	0.19×10^6
Oxygen	O_2	31.6	1.36
Nitrogen	N_2	37.3	1.31
Carbon dioxide	CO_2	42.8	3.61
Carbon monoxide	CO	38.6	1.43
Sulphur dioxide	SO_2	56.5	6.69
Chlorine	Cl_2	46.1	5.35
Hydrogen chloride	HCl	40.9	3.81
Ammonia	NH_3	36.4	4.05
Water	H_2O	33.2	5.87
Ethane	C_2H_6	69.9	6.0
Benzene	C_6H_6	120.3	18.71

* Zeit. phys. Chem. 69, 52 (1910).

It has been pointed out that intermolecular attraction depends not only on the size of the molecules but also on their constitution. Those molecules which are made up of a large number of atoms exert a greater mutual attraction than molecules of the same mass but composed of a smaller number of atoms. This is shown by the data of the foregoing table in which the value of a for ethane, 6.0×10^6, is over four times greater than the corresponding value of a for oxygen, 1.36×10^6, although their molecular weights are nearly the same.

Molecular Diameters. It has been claimed by Richards† that the volume corresponding to the constant b is approximately 1.2 times the volume of one gram-molecule of the liquefied gas

† Jour. Am. Chem. Soc., 36, 629 (1914).

at its boiling-point, and that it may be regarded as representing the actual volume of the molecules themselves. If this be true, we may readily compute the so-called "molecular diameters." To do this, it is only necessary to divide the value of b, expressed in cubic centimeters per gram-molecular weight, by Avogadro's constant, and then extract the cube root of the quotient. The values of the molecular diameters calculated in this manner for several gases are given in the following table, together with the corresponding values computed by means of an equation derived from measurements of the mean free path of a molecule, i.e., from the distance a molecule travels before colliding with another molecule. The agreement between the results obtained by the two methods is most satisfactory.

MOLECULAR DIAMETERS

Substance.	Formula.	Molec. Diam. (from b).	Molec. Diam. (from mean free path).
Hydrogen	H_2	2.34×10^{-8} cm.	2.4×10^{-8} cm.
Oxygen	O_2	2.92	2.97
Carbon dioxide	CO_2	3.23	3.36
Carbon monoxide	CO	3.12	3.19
Nitrogen	N_2	3.15	3.15
Ammonia	NH_3	3.08	2.97

Corresponding States. If, in the equation of van der Waals, the values of p, v and T be expressed as fractions of the corresponding critical values, we may write

$$p = \alpha p_c,$$
$$v = \beta v_c,$$

and

$$T = \gamma T_c.$$

Substituting these values in the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

we have

$$\left(\alpha p_c + \frac{a}{(\beta v_c)^2}\right)(\beta v_c - b) = R\gamma T_c,$$

and replacing p_c, v_c and T_c by their values given in equations (6), (7) and (8), we obtain

$$\left(\alpha + \frac{3}{\beta^2}\right)(3\beta - 1) = 8\gamma, \tag{13}$$

which is known as van der Waals' *reduced equation of state.*

In this equation everything connected with the individual nature of the substance has vanished, thus making it applicable to all substances in the liquid or gaseous state in the same way that the fundamental gas equation is applicable to all gases, irrespective of their specific nature. It has been shown, however, that the equation is not entirely trustworthy and at best can be considered as little more than a rough approximation. The chief point to be observed in connection with this equation is that whereas, for gases, the corresponding values of temperature, pressure and volume, measured in the ordinary units, may be compared, it is necessary in the case of liquids to make the comparison under *corresponding states.* According to van der Waals, two substances are in corresponding states when their pressures are proportional to their critical pressures, their volumes to their critical volumes and their temperatures to their critical temperatures; or, in other words, two substances are in corresponding states when their reduced pressures, volumes and temperatures are equal. The reduced equation of state has been investigated

REDUCED VALUES IN CORRESPONDING STATES

Ratio of Pressure to Critical Pressure = 0.08846

Substance.	T/T_c	V (liquid)$/V_c$	V (gas)$/V_c$
Methyl alcohol	0.7734	0.3973	34.35
Ethyl alcohol	0.7794	0.4061	32.15
Propyl alcohol	0.7736	0.4002	30.85
Methyl acetate	0.7445	0.3989	30.15
Ethyl acetate	0.7504	0.4001	30.25
Propyl acetate	0.7541	0.3985	30.35
Acetic acid	0.7624	0.4100	25.4
Ether	0.7380	0.4030	28.3
Benzene	0.7282	0.4065	28.3
Chlorbenzene	0.7345	0.4028	28.5
Brombenzene	0.7343	0.4024	28.3
Iodobenzene	0.7337	0.4020	28.3

by Young* for about thirty substances at the same reduced pressure, 0.08846. The preceding table is compiled from the data given by Young.

The data of the foregoing table afford ample confirmation of the validity of van der Waals' rule, that: "When the absolute temperatures of two substances are proportional to their absolute critical temperatures, their vapor pressures will be proportional to their critical pressures, and their orthobaric† volumes, both as liquid and vapor, will be proportional to their critical volumes."

Berthelot's Equation. Numerous modifications of the equation of van der Waals have been proposed from time to time, but of these only one need be considered here. As has already been pointed out, a well-defined relation is known to exist between the constants a and b of any particular gas and its critical constants. An equation derived by D. Berthelot,‡ in which a and b are expressed in terms of the critical constants, has been found to represent the behavior of pure gases with a high degree of accuracy over an extended range of pressures. Berthelot's equation may be written in the following form: —

$$pv = RT\left[1 + \frac{9}{128}\frac{p}{p_c}\frac{T_c}{T}\left(1 - 6\frac{T_c^2}{T^2}\right)\right]. \qquad (14)$$

In this equation p_c and T_c are the critical pressure and the critical temperature respectively. Inspection of the equation shows that as T increases or as p decreases, it approaches the simple equation, $pv = RT$, expressing the behavior of an ideal gas. The values of the ratio, pv/RT, calculated by means of equation (14), agree closely with those determined experimentally, provided the gases are neither associated nor dissociated, and that they are sufficiently removed from their critical points.

The most important application of Berthelot's equation is in the precise determination of atomic weights by the physical method (see p. 17). The approximate value of the molecular weight M, of m grams of any gas may be calculated by the equation

$$M = m\frac{RT}{pv}, \qquad (15)$$

* Phil. Mag. V 33, 153 (1892).

† The volume of a liquid at a given temperature and under a pressure equal to the vapor pressure is called the *orthobaric* volume.

‡ Jour. Phys. III 8, 263 (1899).

or, since $d = m/v$, where d is the density of the gas, equation (15) may be written in the form

$$M = d\frac{RT}{p}. \tag{16}$$

If we wish to determine the exact molecular weight of a gas, however, it is necessary to introduce a correction for the deviation from the gas laws. To do this, we make use of the equation of Berthelot instead of the simple equation, $pv = RT$, and obtain the equation

$$M = d\frac{RT}{p}\left[1 + \left\{\frac{9\ T_c(T^2 - 6\ T_c^2)}{128\ p_c T^3}\right\}p\right], \tag{17}$$

or, letting A denote the expression within brackets, we have

$$M = d\frac{RT}{p}(1 + Ap). \tag{18}$$

From this value of M, the exact atomic weight can be calculated by dividing by the number of atoms contained in the molecule. This method of calculating exact atomic weights is known as the "method of critical constants."

Limiting Density. Owing to the fact that the deviation from the simple gas laws becomes less and less as the pressure is lowered, it is evident that the exact value of the molecular weight of a gas can also be calculated directly from its density, provided this can be determined in the neighborhood of zero-pressure. The determination of this so-called "limiting density" can be made with a high degree of accuracy, if the values of the density of the gas at two or more pressures are known.

Let v be the volume of W grams of a gas at 0° C. under a pressure p. The density of the gas per unit of pressure is W/pv. If the gas follows Boyle's law, pv remains constant and the ratio W/pv will likewise remain constant for all pressures, but if the gas deviates from Boyle's law a corresponding deviation will also occur in the ratio W/pv. When $p = 1$, the density of the gas will be normal and, as the pressure is reduced and approaches the limiting value $p = 0$, the density per unit of pressure will approach the value for a perfect gas, i.e., the limiting density. The ratio of

the limiting densities of two gases is equal to the ratio of their molecular weights, or

$$M_a : M_b = \frac{W_a}{(p_0v_0)_a} : \frac{W_b}{(p_0v_0)_b}, \tag{19}$$

where p_0v_0 is the limiting value of pv as p approaches 0 as its limit. If we denote the normal density of a gas by $D = W/p_1v_1$, where p_1v_1 is the value of pv when $p = 1$, then

$$M_a : M_b = D_a\left(\frac{p_1v_1}{p_0v_0}\right)_a : D_b\left(\frac{p_1v_1}{p_0v_0}\right)_b. \tag{20}$$

There are two methods by which the value of the ratio (p_1v_1/p_0v_0) may be determined.

(1) In the case of gases which deviate but slightly from Boyle's law and where the pressure ranges in value from 1 atmosphere down to the limiting value 0, we may assume the relative deviation to be proportional to the pressure, or

$$\frac{(p_0v_0 - pv)}{p_0v_0} = Ap, \tag{21}$$

where A is a constant for each gas at 0° and known as the *coefficient of compressibility*. The value of A may be calculated from Berthelot's equation, p. 63, equation (14), or more simply by determining the value of pv at two pressures between $p = 1$ and $p = 0$. When $p = 1$, $pv = p_1v_1$ and equation (21) reduces to

$$\frac{p_1v_1}{p_0v_0} = 1 - A,$$

or

$$\frac{M_a}{M_b} = \frac{D_a(1 - A_1)}{D_b(1 - A_2)}. \tag{22}$$

(2) In the case of gases which deviate widely from the gas laws, the relative deviation can no longer be assumed to be proportional to the pressure, and the value of p_0v_0 must be determined by extrapolation from a curve in which different values of pv are plotted against the corresponding pressures.

The compressibility coefficients at 0° C. of a few gases are given in the following table:

COEFFICIENTS OF COMPRESSIBILITY AT 0° C.

Oxygen	0.00094	Helium	0.00000
Hydrogen	−0.00053	Carbon monoxide	0.00081
Nitrogen	0.00056	Carbon dioxide	0.00668
Neon	−0.00105	Nitrous oxide	0.00747

Liquefaction of Gases. The history of the liquefaction of gases has for a long time been regarded as one of the most interesting chapters of physical science. Among the first successful workers in this field was Faraday.* He liquefied practically all of the gases which condense under moderate pressures and at not very low temperatures. The apparatus used by Faraday consisted of an inverted V-shaped tube, in one end of which was placed some solid which would liberate the desired gas on heating, while the other end was sealed and immersed in a freezing mixture. When the substance had been heated long enough to liberate considerable gas, the pressure became sufficiently high to cause the gas to liquefy at the temperature of the other end of the tube. Thus, when chlorine hydrate was heated in the tube, the liberated chlorine condensed as a yellow liquid.

In 1834, Thilorier† succeeded in liquefying carbon dioxide in quite large amounts by the use of a new form of apparatus. In connection with his experiments on liquid carbon dioxide, he observed that when it was allowed to vaporize, enough heat was absorbed to lower the temperature below its freezing-point, solid carbon dioxide being obtained. He discovered that a mixture of solid carbon dioxide and ether was a powerful refrigerant, and that under diminished pressure the mixture gave temperatures ranging from −100° C. to −110° C. This mixture is known today as *Thilorier's mixture.*

Faraday‡ undertook the liquefaction of the so-called permanent gases in 1845. In this second series of experiments, he employed higher pressures than in his earlier experiments, and also made use of the newly discovered Thilorier mixture as a refrigerant.

* Phil. Trans., 113, 189 (1823).
† Lieb. Ann., 30, 122 (1839).
‡ Phil. Trans., 135, 155 (1845).

He was partially successful in his attempt to liquefy the hitherto noncondensible gases. He liquefied ethylene, phosphine and hydrobromic acid and also solidified ammonia, cyanogen, and nitrous oxide. He failed to liquefy hydrogen, oxygen, nitrogen, nitric oxide and carbon monoxide. No further advance in the liquefaction of gases was made until the year 1869, when Andrews pointed out the importance of cooling the gas below its critical temperature. This discovery explained why so many of the earlier experiments had failed, and opened the way to the brilliant successes of the latter part of the nineteenth century.

In 1877, Cailletet* and Pictet,† working independently, succeeded in liquefying oxygen. Cailletet subjected the gas to a pressure of about 300 atmospheres using boiling sulphur dioxide as a refrigerant. The gas was further cooled by suddenly releasing the pressure and allowing it to expand. In addition to oxygen he also liquefied air, nitrogen and possibly hydrogen.

Shortly afterward in 1883, the Polish scientists, Wroblewski and Olszewski,‡ published an account of their interesting and highly important work. In their experiments they subjected the gas to be liquefied to high pressure, and simultaneously cooled it to a very low temperature. Among the refrigerants used by them was liquid ethylene, which was allowed to boil off under diminished pressure, giving a temperature of $-130°$ C. At this temperature, a pressure of only 20 atmospheres was sufficient to condense oxygen to the liquid state. Having liquefied oxygen, nitrogen, air and carbon monoxide, and having determined the boiling-points of these gases under atmospheric pressure, they proceeded to use these liquefied gases as refrigerants, allowing them to boil off under diminished pressure, thus obtaining temperatures as low as $-200°$ C. A very small amount of liquid hydrogen was obtained in this way. Subsequent attempts by these same experimenters to liquefy hydrogen, while not much more successful than their former attempts, enabled them to determine its boiling-point. Shortly after the publication of the first papers of Wroblewski and Olszewski, Dewar§ devised a new form of apparatus for lique-

* Compt. rend., 85, 1217 (1877).
† Ibid., 85, 1214, 1220 (1877).
‡ Wied. Ann., 20, 243 (1883).
§ Proc. Roy. Inst., 1886, 550.

fying air, oxygen and nitrogen on a comparatively large scale. He also introduced the well-known vacuum-jacketed flasks and tubes which greatly facilitated carrying out experiments with liquefied gases.

In 1895, Linde in Germany and Hampson in England simultaneously and independently constructed machines for the liquefaction of air in large quantities. In the method devised by these experimenters the air is not subjected to a preliminary cooling, produced by the rapid evaporation of a liquefied gas under diminished pressure, as in the methods of Wroblewski and Olszewski. In the Linde liquefier, the air is compressed to about 200 atmospheres. It is then passed through a chamber containing anhydrous calcium chloride to remove the greater part of the moisture, after which it is cooled by allowing it to circulate through a coiled pipe immersed in a freezing mixture. Nearly all of the moisture remaining in the air is deposited on the walls of the pipe in the form of frost. The air then enters a long spiral tube jacketed with a non-conducting material, and is there allowed to expand to a pressure of about 15 atmospheres. During this expansion the temperature of the air is appreciably lowered. When the air has traversed the spiral tube, it is still further cooled by allowing it to expand to a pressure equal to that of the atmosphere. The air which has been thus cooled is then passed backward through the annular space between the spiral tube and a concentric jacket, thus cooling the entering portion of air. Consequently this next portion of air expands from a lower initial temperature, and the cooling effect is increased. In like manner, when this cooler air passes backward it cools still further the next succeeding portion, and eventually the temperature is reduced sufficiently to cause a small amount of the air to liquefy as it issues from the end of the spiral tube. The remaining portion of the air which has not been liquefied, passes backward through the annular tube and cools the following portion to a still greater extent, causing a larger proportion to liquefy on expansion. With a 3-horse-power machine, a continuous supply of 0.9 liter per hour can be obtained. Further improvements in this apparatus have been made by Dewar and Hampson, and by means of it Dewar's brilliant successes in the liquefaction of gases have been achieved.

The most efficient apparatus for the liquefaction of air and other

is that developed by Claude.* The essential features of his liquefier are shown in Fig. 14. The air is first compressed to 40 atmospheres pressure by means of an ordinary compression pump not shown in the diagram, the moisture and carbon dioxide being removed as in Linde's method. It then enters the tube *A*, which in reality is of a spiral form, and divides at *B*. A portion enters the cylinder *D* through a valve chest similar to that in a steam engine, forcing out the piston and causing the wheel, *W*, to

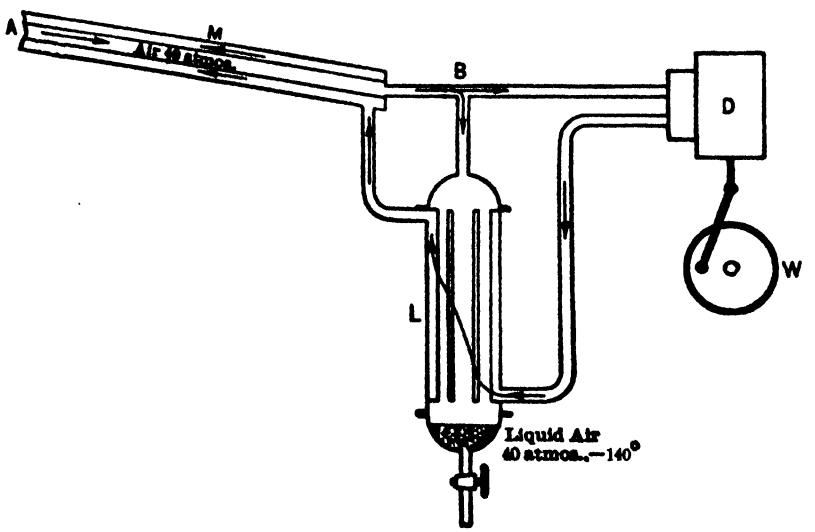

Fig. 14

revolve, thereby doing work and simultaneously cooling the air. The cooled air escapes from the valve chest and circulates through the liquefying chamber *L*, where it causes the portion of compressed air entering at *B* to liquefy. It then issues from the liquefier and traverses *M*, cooling the entering portion of air in *A*, and finally returns to the compressor. The pressure of the air when it issues from *D* is almost atmospheric, but its temperature is below −140° C. About twenty-five per cent of the power consumed in compression is regained by the motor. The apparatus produces about 1 liter of liquid air per horse-power hour. By means of this improved apparatus, based upon the regenerative principle, all known gases have now been liquefied, the last to succumb being

* Compt. rend., II, 500 (1900); I, 1568 (1902); II, 762, 823 (1905).

helium which was liquefied, in 1908, by Kammerlingh Onnes in the Leyden cryogenic laboratory. The subjoined table gives the critical data, together with the boiling and freezing temperatures, of some of the more common gases.

PHYSICAL CONSTANTS OF SOME OF THE PRINCIPAL GASES *

Gas	Density (0°,760mm.)	Crit. Density.	Melting Point.	Boiling Point (760 mm.)	Crit. Temp.	Crit. Press. (Atmos.).
He.....	0.1782	0.07	.....	4.5°Abs.	5.0°Abs.	2.3
H_2.....	0.08987	0.033	14.1° Abs.	20.4	31	13.4
Ne.....	0.9002	.....	30	53	55	29
N_2.....	1.2507	0.311	62.5	77.3	127	33.0
CO.....	1.2504	.....	66	83	133.5	35.5
O_2.....	1.4290	0.162	46	90.1	154.2	50.8
A.....	1.7809	0.509	85.1	87.2	155.6	52.9
NO.....	1.3402	.....	112.5	122.5	179.5	71.2
CH_4.....	0.7168	.....	89	108.3	191.2	54.9
Kr.....	3.708	.....	104	121.3	210.5	54.3
Xe.....	5.851	1.15	133	163	287.7	57.2
CO_2.....	1.9768	0.448	216.3	194.7	304.1	73.0
HCl.....	1.6394	0.41	161.6	189.9	324.8	83.6
NH_3.....	0.7708	.....	194.8	239.5	405.3	109.6
Cl_2.....	3.1674	.....	171.0	239.4	419	93.5
SO_2.....	2.9266	0.513	200.7	263	430.0	78.0
H_2S.....	1.5392	.....	190.0	212.8	373.4	89.3
PH_3.....	1.5293	.....	140.5	186.6	324.3	64.5

* Baumé, Jour. Chim. Phys. 9, 282 (1911).

Separation of Helium from Natural Gas. No treatment of the liquefaction of gases, however brief, should be concluded without mention of the distinctively American industry of separating helium from natural gas on a commercial scale.

Early in the present century the presence of small amounts of the rare gases in certain of the natural gases of Kansas was discovered by Cady. Because of its lightness, non-inflammability and low rate of diffusion through fabrics, helium is an ideal gas for the inflation of balloons and the gas bags of dirigibles. The demand for large quantities of this rare gas for aëronautical purposes during the World War furnished the necessary stimulus for the development of processes whereby the small amounts of helium present in various sources of natural gas could be separated on a commercial scale. A typical sample of one of these natural gases has the composition shown in the following table: —

	Per cent
Helium	0.93
Carbon dioxide	0.25
Oxygen	0.54
Methane	56.85
Ethane and heavier hydrocarbons	10.30
Nitrogen	31.13
	100.00

The process of separation involves the liquefaction of all of the gases present in the mixture except the helium, followed by a process of purification of the latter in which the percentage of helium is increased from about 70 to over 90 per cent. In the Claude process, which is one of several different processes employed, the natural gas is taken from the gas-holder at atmospheric pressure and led through a train of scrubbers to remove the carbon dioxide. The gas, freed from carbon dioxide, then enters the separators in which a large proportion of the moisture is removed. From the separators it is led to the compressor where the pressure is raised to approximately 600 lbs. per sq. in. The gas then passes through the coolers where the heat developed by compression is removed and then at atmospheric temperature it enters the oil removers. After the removal of the oil, it passes through a battery of driers containing granular calcium chloride to remove the last traces of moisture. The gas now enters the interchangers where the incoming current of gas meets the returning previously cooled gas. After traversing the interchangers, 25 per cent of the gas is run through a liquefier, while the other 75 per cent is expanded through a small expansion engine from the initial 600 lbs. pressure down to 120 lbs. The gas which issues from the expansion engine is partially liquefied after traversing a train of condensers, the last member of which is cooled by the expansion of a mixture of liquefied methane and nitrogen. The last traces of methane are practically completely removed at this point as well as a large proportion of the nitrogen. The helium together with the residual unliquefied nitrogen is then collected in a large reservoir from which it can be subsequently removed for purification.*

* For an excellent detailed account of the commercial preparation of helium the student should read the comprehensive article on this subject written by Dr. R. B. Moore in the Journal of the Franklin Institute, 191, 145 (1921).

Vapor Pressure of Liquids. According to the kinetic theory there is a continuous flight of particles of vapor from the surface of a liquid into the free space above it. At the same time the reverse process of condensation of vapor particles at the surface of the liquid is taking place. Eventually a condition of equilibrium will be established between the liquid and its vapor, when the rate of escape will be exactly counterbalanced by the rate of

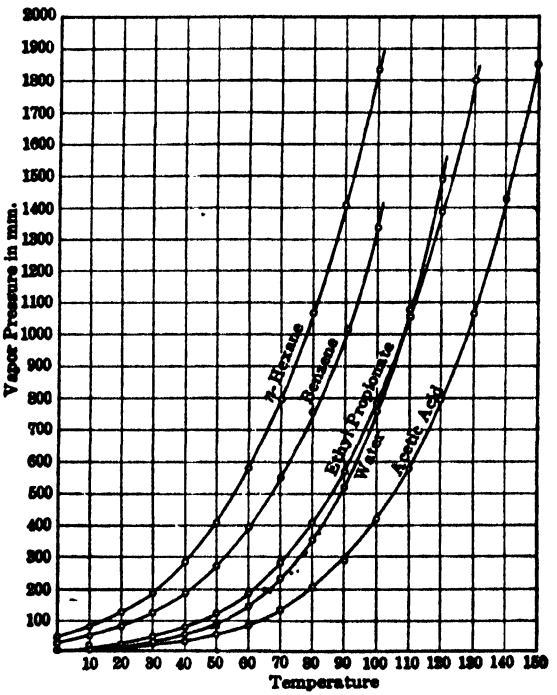

Fig. 15

condensation of vapor particles: the vapor is then said to be *saturated*. The pressure exerted by the vapor of a liquid when equilibrium has been attained is known as its *vapor pressure*. The equilibrium between a liquid and its vapor is dependent upon the temperature. For every temperature below the critical temperature, there is a certain pressure at which vapor and liquid may exist in equilibrium in all proportions; and conversely for every pressure below the critical pressure, there is a certain temperature at which vapor and liquid may exist in equilibrium in all propor-

tions. This latter temperature is termed the boiling-point of the liquid in the special case where the pressure is 760 mm. The vapor pressure of a liquid is a constant quantity, but it increases as the temperature is raised and is independent of the amounts of liquid and vapor present. The following table gives the vapor pressures of several typical liquids from 0° to 100°C.

VAPOR PRESSURES

Temp.	Water	Acetic acid	Ethyl propionate	n-Hexane	Benzene
0°	4.60 mm.	3 30 mm.	8 30 mm.	45 45 mm.	26 54 mm.
10	9.16	6 38	15 55	75 00	45.43
20	17 39	11 73	27 75	120 0	74.66
30	31.55	20 61	47.75	185 4	118.24
40	54 91	34 77	77 9	276 7	181.08
50	91.98	56 56	123.0	400 9	268.97
60	148.79	88 94	188 0	566.2	388.58
70	238 06	136 0	279 9	787.0	547.40
80	354.62	202.3	403 6	1062.	735 62
90	525.39	293 7	569.5	1407.	1016.1
100	760 00	417.1	785.0	1836	1344.3

The data of the foregoing table are represented graphically in Fig. 15.

Relation between Vapor Pressure and Temperature. While the exact relation between the temperature and the pressure of the vapor of a liquid is not known, yet a large number of empirical formulæ have been derived expressing this relationship in terms of arbitrary constants. Several of these empirical formulæ have proven very useful. The first attempt to correlate vapor pressure and temperature was made by Dalton,* who suggested that the vapor pressure of a liquid increases in geometrical progression as the temperature increases in arithmetical progression. Dalton's generalization may be expressed mathematically as follows:

$$\log p = bt + c, \tag{23}$$

where p and t denote the vapor pressure and temperature respectively and where b and c are constants. This formula has been

* Dalton, Mem. Manchester Lit. Phil. Soc., 5, 550 (1801).

found to hold only within narrow limits of temperature near the point at which b and c were determined.

A more satisfactory equation, proposed by Young, has the form

$$\log p = A + B/T, \tag{24}$$

where A and B are constants and T is the absolute temperature. If two different substances have the same vapor pressure, p, at the two absolute temperatures, T' and T'' respectively, it follows from equation (24) that

$$\log p = A' + B'/T' = A'' + B''/T'',$$

or

$$\frac{T'}{T''} = \frac{1}{B''}[B' + (A' - A'')T']. \tag{25}$$

It is apparent that the ratio of the absolute temperatures at which the two substances have the same vapor pressure, is a linear function of the temperature T' of one of the substances. If the constants, A and B, of a standard substance be evaluated by measuring its vapor pressure at two different temperatures, Ramsay and Young have shown that equation (25) may be employed to deduce the vapor pressure of an unknown substance.

Probably the most valuable of the many empirical vapor pressure formulæ which have been proposed is that first derived by Kirchhoff* in 1858, and subsequently by Rankine in 1866. This equation, sometimes known as the Kirchhoff formula and more often as the Rankine formula, may be written in the form,

$$\log p = \frac{A}{T} + B \log T + C, \tag{26}$$

where A, B and C are constants. This formula has been found to apply to a large variety of substances up to the critical temperature with a maximum error not exceeding three per cent. It should be pointed out that while the formulæ of Young and Kirchhoff are empirical, nevertheless both of them are derivable from fundamental thermodynamic relations, provided certain reasonable assumptions are made.

An inspection of equations (24) and (26) reveals the fact that the logarithm of the vapor pressure of a liquid is very nearly a

* Kirchhoff, Pogg. Ann. 103, 185 (1858).

linear function of the reciprocal of its absolute temperature. The validity of this statement is borne out by the curves shown in Fig. 16 which represent the logarithms of the vapor pressures given in the table on p. 73 plotted as functions of the reciprocals of the corresponding absolute temperatures.

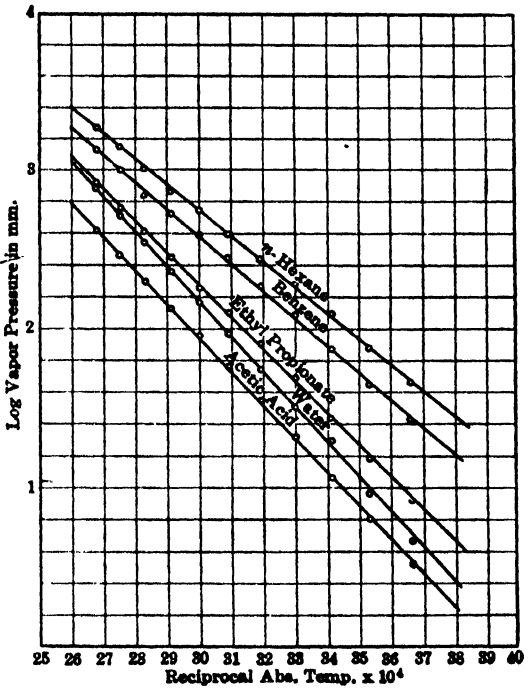

Fig. 16

Measurement of Vapor Pressure. The vapor pressure of a liquid may be measured directly by placing a portion of it above the mercury in the vacuum of a barometer tube, heating to the desired temperature, and observing the depression of the mercury column. This is known as the *static method*. It is open to the objection that the presence of volatile impurities in the liquid causes too great depression of the mercury column, the vapor pressure of the impurity adding itself to that of the liquid whose vapor pressure is sought. A better method for the measurement of vapor pressure is that known as the *dynamic method*. In this method, the pressure is maintained constant and the boiling temperature is determined with an accurate thermometer. The boiling temperatures corresponding to various pressures may be measured, provided we have a suitable device for changing and measuring the pressure. The results obtained by the static and dynamic methods agree closely if the liquid is pure, but if volatile impurities are present the results obtained by the dynamic method are more trustworthy. A method for the measurement of vapor pressure due to James

Walker* is of considerable interest. In this method, a current of pure dry air is bubbled through a weighed amount of the liquid whose vapor pressure is to be determined. The liquid is maintained at constant temperature and its loss in weight is observed. In passing through the liquid, the air will absorb an amount of vapor directly proportional to the vapor pressure of the liquid. If 1 mol of liquid is absorbed by v liters of air, then we have

$$pv = RT,$$

where p is the vapor pressure of the liquid, and T its temperature. If v_1 is the volume of air which absorbs g grams of the vapor of the liquid whose molecular weight is M, then

$$pv_1 = \frac{g}{M} RT,$$

or

$$p = \frac{g}{Mv_1} RT. \tag{27}$$

In this equation, v_1 denotes the total volume containing g grams of the liquid in the form of vapor, or in other words it represents the air and vapor together. Since the volume of the air is, in general, so much greater than that of the vapor, v_1 may be taken as that of the air alone.

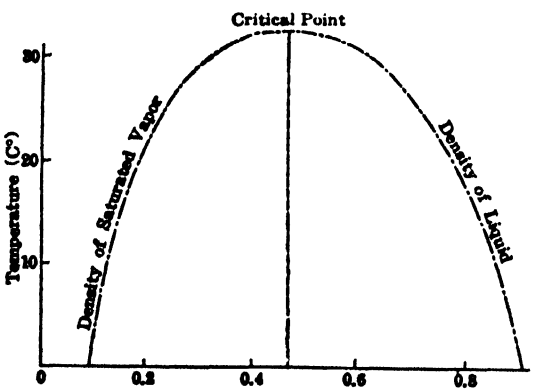

Fig. 17

Other methods for measuring vapor pressure will be considered in a later chapter.

Law of Cailletet and Mathias. If the densities of a liquid and its saturated vapor are plotted against temperature, a curve of the form shown in Fig. 17 is obtained. This curve shows that as the temperature is raised the densities of the liquid and vapor phases

* Zeit. phys. Chem., 2, 602 (1888).

approach each other and, at the critical temperature, become equal. Cailletet and Mathias* pointed out that the mean of the densities of any substance in the state of liquid and saturated vapor, when plotted against the corresponding temperatures, lie on a straight line. If d_l and d_v denote the densities of liquid and vapor respectively, the relation of Cailletet and Mathias may be expressed mathematically by the equation,

$$\frac{d_l + d_v}{2} = a + bT, \tag{28}$$

where a and b are constants. This relation is sometimes called the law of the *rectilinear diameter*. It holds fairly well for a number of substances, but with others it is found that the mean of the densities of the two phases is not strictly a linear function of the temperature. In general it may be said that the relation holds in the immediate vicinity of the critical temperature better than at lower temperatures. The law of Cailletet and Mathias has proven useful in determining the value of the critical density, a quantity which frequently cannot be measured directly.

Boiling-Point and Critical Temperature. An interesting relation has been pointed out by Guldberg† and Guye.‡ These two investigators have shown that the absolute boiling temperature of a liquid is about two-thirds of its critical temperature. That this empirical relation holds for a variety of different substances is shown in the accompanying table.

RELATION OF BOILING-POINT TO CRITICAL TEMPERATURE

Substance.	T_b	T_c	T_b/T_c
Oxygen	90°	155°	0.58
Chlorine	240°	414°	0.58
Sulphur dioxide	263°	429°	0.61
Ethyl ether	308°	467°	0.66
Ethyl alcohol	351°	516°	0.68
Benzene	353°	562°	0.63
Water	373°	637°	0.59
Phenol	454°	691°	0.66

* Compt. rend. 102, 1202 (1886); 104, 1563 (1887).

† Zeit. phys. chem., 5, 376 (1890).

‡ Bull. Soc. Chim., (3), 4, 262 (1890).

The Law of Ramsay and Young. It was pointed out by Ramsay and Young* that if the absolute boiling-points of two closely related liquids, A and B, are compared under equal pressures, the following relation will be found to hold: —

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} + c(T'_A - T_A), \tag{29}$$

where T_A and T_B are the absolute boiling-points of A and B under the same pressure, T'_A and T'_B the corresponding boiling-points under another pressure, and c is a constant. This relation has been shown to be valid from very low pressures up to the critical pressure. The constant c is practically zero for the majority of closely related liquids. The law of Ramsay and Young has been found very useful in estimating the values of the boiling-points of different liquids over a range of pressures, the corresponding variation in boiling-point of a closely related liquid being taken as a standard of comparison. Furthermore, variation in the value of the constant c may be used as a criterion of abnormality in the molecular state of liquids. A law similar to that of Ramsay and Young has recently been shown by Creighton† to apply to fluidity, surface tension and reaction pressure.

Heat of Vaporization. In order to transform a liquid into a vapor, a large amount of heat is required. Thus, when a liquid is heated to the boiling-point, the volume must be increased against the pressure of the atmosphere, external work being done, and when the boiling temperature is reached, the liquid must be vaporized. The heat expended in causing the change of physical state is much greater than that required to expand the liquid. The heat required to convert one gram of a liquid at the boiling point into vapor at the same temperature is known as the heat of vaporization of the liquid.

Undoubtedly the most satisfactory method for the determination of heats of vaporization is that recently developed by Mathews.‡ In this method the amount of electrical energy required to vaporize a given weight of the liquid, the heat of vaporization of which is sought, is accurately measured and the equivalent in thermal units is calculated.

* Phil. Mag. V **20**, 515 (1885); **21**, 33 (1886); **22**, 37 (1886).

† Jour. Franklin Inst., **193**, 647 (1922).

‡ Mathews, Jour. Am. Chem. Soc., **48**, 562 (1926).

The general arrangement of the apparatus is shown in Fig. 18. The vaporizer *B*, containing the liquid whose heat of vaporization is to be determined, is a small glass tube, 26 mm. in diameter and 125 mm. long. At the top it is constricted to a small orifice 3 mm. in diameter. A reflecting surface, obtained by coating the outside of the vessel with silver, aids materially in

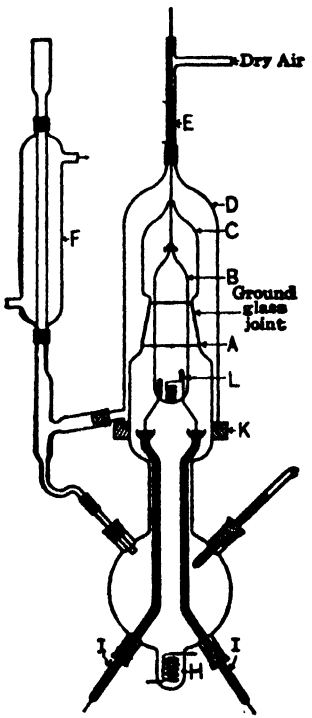

Fig. 18

preventing heat exchange to or from the vessel by radiation. Two heavy platinum wires *L*, sealed into the base of the vaporizer, serve as terminals of the heating coil. These two heavy platinum wires dip into mercury cups, in order to complete the electrical circuit. The heating coil (resistance 5 to 8 ohms) consists of a helix of fine platinum wire set in a vertical position. It is supported on a light mica frame, not shown in the diagram.

Two small platinum wires sealed into the neck of the vaporizer (forming small hooks) afford a means of attaching the vaporizer to

a fine brass suspension wire, which leads to one arm of an analytical balance placed above the entire apparatus. The vessel at the bottom serves as a boiler for the generation of the vapor used to jacket the vaporizer. This is sealed onto the chamber, *A*, in which the vaporizer is suspended. Some of the same liquid as that contained in the vaporizer is placed in the boiler and a current of from 6 to 8 amperes is passed through the resistance coil in the cistern, *H*, at the bottom of the boiler.

The cap, *C*, also is constricted at the top and has a 3 mm. hole for the passage of the suspension wire. The outer vessel, *D*, consists of a large cylindrical tube open at the bottom and constricted at the top, with an orifice 3 mm. in diameter. By means of a tubulure on the boiler, connection is made with the condenser *F*. The outer vessel, *D*, rests in an annular ring of mercury contained in a channel cut in the cork *K*, and this vessel is also connected to the return condenser. The mercury seal prevents vapor from escaping from the outer vessel *D*.

Electrical contact with the terminals of the heating element in the vaporizer and the outside circuit is furnished through the two tubes, *I*, which are filled with mercury. Heavy amalgamated platinum wires, sealed into the lower ends of these tubes, extend into mercury cups providing contact with the outside electrical circuit. The upper ends of the tubes, *I*, are flanged out into cups 13 mm. in inside diameter, thus providing a fairly flat surface of mercury into which dip the platinum wires, *L*, from the vaporizer.

The brass suspension wire, as it emerges from the outer vessel *D*, leads up through the center of a coil of manganin resistance wire, encased in the glass " chimney " *E*. By passing from 1 to 2 amperes of current through this heating coil, condensation on the suspension wire is prevented. To prevent the escape of vapor from the " chimney," *E*, a slow current of dry air is drawn into the apparatus by means of an aspirator bottle attached to the condenser *F*. An excess of dry air is passed into the " chimney " under slight pressure, the excess not needed passing out at the top. This procedure prevents loss of vapor and also at the same time prevents condensation of liquid on the suspension wire.

In carrying out a determination the experimental liquid is pipetted into the vaporizer as quickly as possible; a small capillary tube closed at the upper end is also introduced into the vaporizer

to prevent bumping of the liquid when it starts to boil, and the apparatus is again assembled, as shown in Fig. 18. Approximately 100 cc. of the same liquid is placed in the boiler. By means of a swivel and turnbuckle attached to the suspension wire, the vaporizer is so adjusted that the copper "contactors" suspend directly into the center of the mercury cups to a depth of about 4 mm. and the ends of the platinum electrodes suspend about 0.5 mm. above the surface of the mercury. The wooden frame supporting the apparatus is then so adjusted that the suspension wire hangs free and does not touch at any point. As soon as the proper alignment is attained, the liquid in the boiler is made to boil, the vapor rises and surrounds the vaporizer, passes out of the orifice at the top of the cap *C*, down through the space between *C* and *D* and out of the tubulure at the bottom of *D* to the condenser, where it condenses and flows back to the boiler through a trap. The return of material to the boiler is important for two reasons. It saves material and prevents possible slight changes in temperature which would result from a fractionation effect which would be experienced were the liquid not quite pure. In a few minutes the temperature of the liquid in the vaporizer is brought to the boiling point, the switch connecting the heating element of the vaporizer is closed, and the rheostat in the circuit adjusted so that about 1 ampere of current flows through the heating coil. The current is then brought to exactly 1 ampere by means of a sliding manganin wire. Several measurements of the potential drop across the blocks are then made while exactly 1 ampere of current flows through the heating coil. Sufficient weights are now placed on the balance pan to balance the weight of the vaporizer and confined liquid and a 1 g. weight is removed. The pointer of the balance is then set so as to coincide with the third small mark on the balance scale. When the pointer swings across the zero mark of the scale the chronometer is started. A 10 g. weight is now removed from the balance pan and the pointer returns to its original position on the scale. The current is held constantly at *exactly* 1 ampere during the entire period required to evaporate 10 g. of liquid from the vaporizer. Any fluctuations in the current are immediately compensated by the operator, who constantly watches the spot of light on a galvanometer scale on the wall. When the balance pointer again swings past the zero mark the run is finished and the time is

recorded. It will be noted that the liquid in the vaporizer is boiled for some time before the actual distillation of the 10 g. sample. This is important as this procedure insures the removal of any dissolved air.

Sufficient data are thus obtained for the calculation of the latent heat of vaporization of the liquid from the formula, $Q = (R \times T \times I^2)/(W \times 4.186)$, where R is the resistance of the heating element (which has been previously determined), T the time necessary to evaporate W grams of liquid and I the current strength measured in amperes.

Trouton's Relation. An interesting relation between the heat of vaporization and the absolute boiling-point of a liquid was discovered by Trouton.* If T denotes the absolute boiling-point and L_v, the heat of vaporization of 1 gram of liquid whose molecular weight is M, then according to Trouton,

$$\frac{ML_v}{T} = 21, \tag{30}$$

or in words, the ratio of the molecular heat of vaporization to the absolute boiling temperature of a liquid is constant, the numerical value of the ratio being approximately 21. This is known as Trouton's law. While this relation holds quite well for many liquids, Nernst has pointed out that the constant varies with the temperature, and has proposed two other forms of the equation. Bingham has simplified the equations of Nernst to the following form: —

$$\frac{ML_v}{T} = 17 + 0.011\ T. \tag{31}$$

While this modification of the Trouton equation has been found to hold for a large number of substances, there are other substances for which the left side of the equation has a value greater than that of the right side. Bingham infers that where this occurs, the substance in the liquid state has a greater molecular weight than it has in the gaseous state, or in other words, the liquid is associated. It is evident that an associated liquid will require an expenditure of energy over and above that required for vapori-

* Phil. Mag. (5), 18, 54 (1884).

sation, to break down the molecular complex. The difference between the values of the two sides of the equation may be taken as a rough measure of the degree of association.

The Internal Pressure of Liquids. The importance of allowing for the existence of attractive forces acting between the molecules of gases becomes more and more evident as the pressure is increased. As has been pointed out, the term a/v^2, was introduced by van der Waals into the equation expressing the simple gas laws to correct for this intermolecular attraction. If such attractive forces did not exist, it is obvious that much larger pressures would be required to bring about the liquefaction of gases than is actually the case. For example, it may be shown that if no attractive forces were operative between the molecules of water vapor, the pressure required to condense one gram-molecule of vapor into the volume occupied by one gram-molecule of liquid water, at room temperature, would be over 1300 atmospheres. The pressure required to condense one gram-molecule of a substance in the gaseous state to the volume occupied by one gram-molecule in the liquid state, in the absence of intermolecular attraction, is called the *internal pressure* of the liquid. The ultimate cause of intermolecular attraction is still a matter of conjecture and, although numerous equations have been derived for the calculation of the internal pressure of liquids, the results thus far obtained are not entirely satisfactory. The following table gives the values of the internal pressure of a few liquids as calculated by four different methods.

INTERNAL PRESSURE OF LIQUIDS *

Temp. 20°

Substance	$P_{\dagger}$	$P_{\ddagger}$	$P_{\S}$	$P_{\parallel}$
Ether	1240 atmos.	1600 atmos.	2590 atmos.	930 atmos.
Carbon tetrachloride	1600	2080	3480	1190
Benzene	1770	2360	3810	1300
Carbon disulphide	2260	3040	3840	1920

* Hildebrand, Jour. Am. Chem. Soc., 41, 1071 (1919).

† From heat of vaporization.

‡ From critical data.

§ From coefficients of expansion and compressibility

‖ From coefficient of expansion.

Surface Tension. The attraction between the molecules of a liquid manifests itself near the surface where the molecules are subject to an unbalanced internal force. The condition of a liquid near its surface is roughly depicted in Fig. 19, where the dots A, B, and C represent molecules and the circles represent the

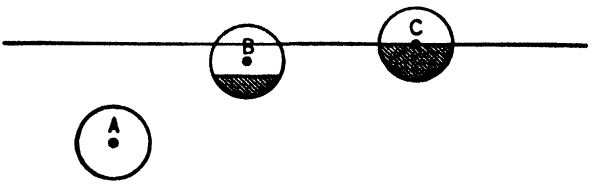

Fig. 19

spheres within which lie all of the other molecules which exert an appreciable attraction upon A, B, and C. The shaded portions represent those molecules whose attractions are unbalanced. These unbalanced forces will evidently tend to diminish the surface to a minimum value. That is, the contraction of the surface of a liquid involves the expenditure of energy by the liquid. The surface film of a liquid is consequently in a state of tension.

Some liquids wet the walls of a glass capillary tube while others do not. When the liquid wets the tube, the surface is concave and the liquid rises in the tube; on the other hand, when the liquid does not adhere, the surface is convex and the liquid is depressed in the tube. The law governing the elevation or depression of a liquid in a capillary tube was discovered by Jurin and may be stated thus: — *The elevation or depression of a liquid in a capillary tube is inversely proportional to the diameter of the tube.* Let a capillary tube of radius r, as shown in Fig. 20, be immersed in a vessel of liquid whose density is d, and let the elevation of the liquid in the capillary be denoted by h. Then the weight of the column of liquid in the capillary will be $\pi r^2 hdg$, where g is the acceleration due to gravity. The force sustaining this weight is the vertical component, $2\pi r\gamma\cos\theta$, of the force due to the tension

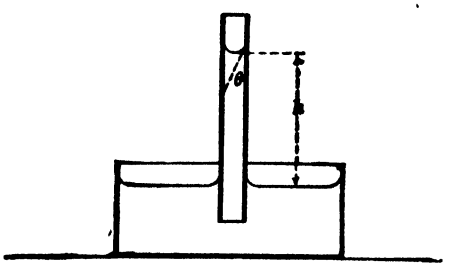

Fig. 20

of the liquid surface at the walls of the tube, γ being the surface tension and θ the angle of contact of the liquid surface with the walls of the tube.

Therefore

$$\pi r^2 hdg = 2\pi r\gamma \cos\theta,$$

or

$$\gamma = \frac{hdgr}{2\cos\theta}.$$

In the case of water and many other liquids θ is so small that we may write $\theta = 0$, the foregoing expression becoming

$$\gamma = 1/2\, h\, dgr. \qquad (32)$$

Thus the surface tension of a liquid can be calculated provided its density and the height to which it rises in a previously calibrated tube is known. When h and r are expressed in centimeters, γ will be expressed in dynes per centimeter or ergs per square centimeter.

A simple form of apparatus for the determination of surface tension used by the author is shown in Fig. 21. A capillary tube, *A*, of uniform bore is sealed to a glass rod, *E*, which is held in position in the test tube, *B*, by means of a cork stopper. A short right-angled tube, *D*, and a thermometer, *F*, are also passed through the same cork stopper. The liquid whose surface tension is to be measured is introduced into the tube, *B*, the cork inserted and the tube placed inside of the larger tube, *C*, containing a liquid of known boiling-point. When the thermometer, *F*, has become stationary, the capillary elevation of the liquid is measured with a cathetometer. The tube, *D*, permits the escape of vapor from the liquid in *B* and at the

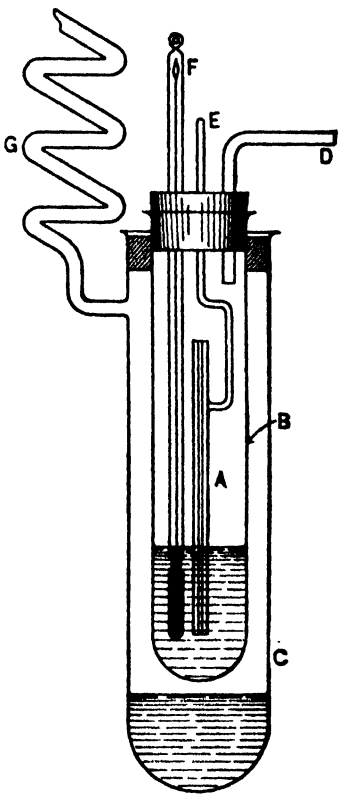

Fig. 21

same time insures equality of pressure inside and outside of the apparatus. The spiral tube, G, serves as an air condenser, preventing loss of vapor from the liquid in the outer tube. The surface tension of a liquid has been found to depend upon the nature of the liquid and also upon its temperature.

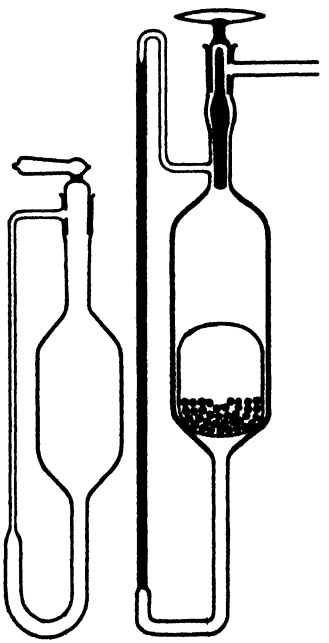

Fig. 22

It has recently been shown by Richards and Coombs*, that the values of the surface tension of liquids as determined by the capillary method, are in error, owing to the fact that the values of h, in equation (24), as ordinarily measured, are slightly less than the true values of h, when measured from a strictly horizontal surface. To avoid this source of error, Richards and Coombs devised the apparatus shown in Fig. 22, where the larger tube has a sufficient diameter (38 mm.) to secure a perfectly flat surface. The height to which a liquid rises in the capillary tube is measured by means of a cathetometer: the difference between the reading of the telescope when focussed, (1) on the capillary meniscus and, (2) on the horizontal surface in the wide tube, is the true capillary rise, h.

Surface Tension and Molecular Weight. In 1886, Eötvös† showed that the surface tension multiplied by the two-thirds power of the molecular weight and specific volume is a function of the absolute temperature, or

$$\gamma\,(Mv)^{\frac{2}{3}} = f\,(T),$$

where γ is the surface tension, M the molecular weight, v the specific volume or reciprocal of the density, and T the absolute tem-

* Jour. Am. Chem. Soc., 37, 1656 (1915).

† Wied. Ann., 27, 448 (1886).

perature. Ramsay and Shields* modified the equation of Eötvös as follows: —

$$\gamma (Mv)^{\frac{2}{3}} = k (t_c - t - 6), \qquad (33)$$

t_c being the critical temperature of the liquid, t the temperature of the experiment, and k a constant independent of the nature of the liquid. The physical significance of the two-thirds power of the molecular volume has been explained by Ostwald in the following manner: — Assuming the molecules to be spherical, we shall have for two different liquids, the proportion

$$V_1 : V_2 :: r_1^3 : r_2^3,$$

where V_1 and V_2 represent the volumes and r_1 and r_2 the radii of their respective molecules. Similarly the ratio of the surfaces, S_1 and S_2, of the molecules in terms of their respective radii, will be

$$S_1 : S_2 :: r_1^2 : r_2^2.$$

From these two proportions it follows that the ratio of the molecular surfaces in terms of the molecular volumes, will be

$$S_1 : S_2 :: V_1^{\frac{2}{3}} : V_2^{\frac{2}{3}}.$$

Making use of the value of M as determined in the gaseous state, Ramsay and Shields found the value of k for a large number of liquids to be equal to 2.12 ergs. Among the liquids for which this value of k was found, were benzene, carbon tetrachloride, carbon disulphide and phosphorus trichloride. For certain other liquids, such as water, methyl and ethyl alcohols and acetic acid, k was found to have values much smaller than 2.12. Ramsay and Shields attributed these abnormalities to an increase in molecular weight due to association, and suggested that the degree of association might be calculated from the equation

$$x^{\frac{2}{3}} = 2.12/k',$$

or

$$x = \left(\frac{2.12}{k'}\right)^{\frac{3}{2}}, \qquad (34)$$

where x denotes the factor of association, and k' is the value of the constant for the associated liquid in equation (33). It was further pointed out by Ramsay and Shields that equation (33)

* Zeit. phys. Chem., 12, 431 (1893).

affords a means of calculating the molecular weight of a pure liquid, provided we assume that the mean value of k is 2.12 for a non-associated liquid. Since it is not an easy matter to determine the critical temperature with accuracy, Ramsay and Shields made use of a differential method, and thus eliminated t_c from equation (33). If the surface tension of a liquid be measured at two temperatures t_1 and t_2, and the corresponding densities are d_1 and d_2, we shall have

$$\gamma_1 (M/d_1)^{\frac{2}{3}} = k (t_c - t_1 - 6), \tag{35}$$

and

$$\gamma_2 (M/d_2)^{\frac{2}{3}} = k (t_c - t_2 - 6). \tag{36}$$

Subtracting equation (28) from equation (27), we obtain

$$\frac{\gamma_1 (M/d_1)^{\frac{2}{3}} - \gamma_2 (M/d_2)^{\frac{2}{3}}}{t_2 - t_1} = k = 2.12, \tag{37}$$

or solving equation (37) for M, we have

$$M = \left(\frac{k d_1^{\frac{2}{3}} \cdot d_2^{\frac{2}{3}} \cdot (t_2 - t_1)}{\gamma_1 d_2^{\frac{2}{3}} - \gamma_2 d_1^{\frac{2}{3}}} \right)^{\frac{3}{2}}.$$

The method of Ramsay and Shields is the best known method for the determination of the molecular weight of a pure liquid.

If M is known to be the same in the liquid and gaseous states, or in other words, if k is independent of the temperature, even though its value is not exactly 2.12, the critical temperature of the liquid can be calculated by means of equation (33). In order that the correct value of the critical temperature may be obtained, Ramsay and Shields found it necessary to use the specific value of k for the liquid whose critical temperature is sought. As an illustration of the method of calculation, the following example is taken from the work of Ramsay and Shields.

For carbon disulphide,

γ at 19°.4 = 33.58,	γ at 46°.1 = 29.41,
d at 19°.4 = 1.264,	d at 46°.1 = 1.223.

We have then for $\gamma (M/d)^{\frac{2}{3}}$, at the two temperatures,

$$(76/1.264)^{\frac{2}{3}} \times 33.58 = 515.4,$$

and

$$(76/1.223)^{\frac{2}{3}} \times 29.41 = 461.4.$$

Substituting in the equation

$$\frac{\gamma_1 (M/d_1)^{\frac{2}{3}} - \gamma_2 (M/d_2)^{\frac{2}{3}}}{t_2 - t_1} = k,$$

we have,

$$\frac{515.4 - 461.4}{46.1 - 19.4} = 2.022.$$

This value of k is so nearly equal to the mean value, 2.12, that we assume M to be the same in the liquid and gaseous states, and therefore we may substitute in equation (1) and calculate the critical temperature of carbon disulphide thus,

$$\gamma (M/d)^{\frac{2}{3}} = k (t_c - t - 6),$$

or solving for t_c, we have

$$t_c = \frac{\gamma (M/d)^{\frac{2}{3}}}{k} + t + 6.$$

Substituting the data given above, in the preceding equation, we obtain

$$t_c = 515.4/2.022 + 6 + 19.4,$$

or $t_c = 280°.3$ C.

Surface Tension and Drop-Weight. Morgan and his co-workers,* from measurements of the volumes of a single drop falling from the carefully-ground tip of a capillary tube, have shown that the weight of the falling drop from such a tip can be used in place of the surface tension in the equation of Ramsay and Shields for the calculation of molecular weights and critical temperatures. The modified equation may be written thus: —

$$\frac{w_1 (M/d_1)^{\frac{2}{3}} - w_2 (M/d_2)^{\frac{2}{3}}}{t_2 - t_1} = k, \qquad (38)$$

where w_1 and w_2 are the respective weights of the falling drop at the temperatures, t_1 and t_2. The value of k obviously depends upon the tip employed.

The results obtained by the drop-weight method have been shown to be more trustworthy than those obtained by the method of capillary elevation. Morgan has further pointed out that

* Jour. Am. Chem. Soc., 30, 360 (1908); 30, 1055 (1908). See also papers by Harkins (Jour. Am. Chem. Soc. 39, 572 (1917) and Lohnstein Z. phys. Chem. 84, 410 (1913).

when the experimental data are substituted in the preceding formula, the magnification of the experimental errors is appreciably greater than when use is made of the original formula,

$$w\,(M/d)^{\frac{1}{3}} = k\,(t_c - t - 6). \qquad (39)$$

Morgan recommends therefore that this formula be used for the determination of molecular weights. After having calibrated a particular tip with pure benzene (a liquid which is known to be non-associated), and thus ascertaining the value of k, the drop-weights at several different temperatures are determined. If we assume M to have the same value in the liquid and gaseous states, the value of t_c can be computed by substituting the experimental data in the preceding equation. If at the different temperatures at which drop-weights are determined, the same value of t_c is obtained, then we may infer that the liquid is non-associated and, therefore, that the assumption made as to the value of M is confirmed. It is a singular fact that the calculated value of t_c for some liquids does not agree with the experimental value, although it remains constant throughout an extended range of temperatures. Morgan considers a constant value of t_c to be an indication of non-association, even if the value is fictitious. In this method the constancy of the calculated value of the critical temperature becomes the criterion of molecular association and thus affords a means of determining whether the molecular weight in the liquid state is identical with that in the gaseous state. The values of t_c calculated from the drop-weights of an associated liquid become steadily smaller as the temperature increases. A large number of liquids have been studied by this method, and the results indicate that many of the substances which were considered to be associated by Ramsay and Shields are in reality non-associated; in fact, it appears from the work of Morgan that association is much less common among liquids than has hitherto been supposed.

Viscosity. The resistance experienced by one portion of a liquid in moving over another portion is called *viscosity*. The viscosity of liquids varies greatly, some liquids, such as ether, being very mobile, while others, such as tar, are extremely viscous. It has been shown experimentally that the tangential force, f, required to maintain a constant difference between the velocities of two parallel layers of liquid moving in the same direction varies

directly with the difference in velocity, u, and the area, A, of the surface of contact of the two layers, and inversely as the distance, d, between the layers. That is,

$$f = \eta \frac{Au}{d}, \tag{40}$$

where η, is a proportionality factor known as the *coefficient of viscosity*. The unit of viscosity is the *poise:* this may be defined as that viscosity which a liquid possesses when a force of one dyne is necessary to cause two parallel liquid surfaces of unit area and unit distance apart to slide past one another with unit velocity. The viscosity of a liquid is generally measured by observing the time required for a definite volume of liquid to flow through a standardized capillary tube under a known difference of pressure. The law governing the flow of liquids through capillary tubes was discovered by Poiseuille* and may be expressed by the equation

$$\eta = \frac{\pi P r^4}{8 V l} t, \tag{41}$$

in which V denotes the volume of liquid of viscosity η, flowing through a capillary tube of length l, and radius r, in the time t, and under the pressure P. If the times of flow of equal volumes of two liquids through the same capillary are measured under the same driving pressure, it follows from equation (41) that

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}, \tag{42}$$

where η_1 and η_2 denote the coefficients of viscosity of the two liquids, d_1 and d_2 their densities and t_1 and t_2 their times of flow. If a liquid of known viscosity be selected as a standard, equation (42) may be used to calculate the so-called "relative viscosity" of other liquids. Water is quite generally accepted as the standard of reference in determinations of relative viscosity. In calculating the relative viscosity of a liquid referred to water, therefore, we employ the following equation:

$$\frac{\eta_1}{1} = \frac{d_1 t_1}{d_w t_w}, \tag{43}$$

in which η_1, d_1 and t_1 denote the viscosity, density and time of flow, respectively, of the liquid under investigation, and d_w and t_w

* Ann. Chim. Phys., 37, 50 (1843).

denote the density and time of flow of water. Relative viscosities may be transformed into absolute viscosities by multiplying the relative viscosity by the absolute viscosity of water at the same temperature as that at which the measurements are made.

A convenient type of viscometer is shown in Fig. 23. The liquid is allowed to flow under its own pressure through the capillary *db*. An accurately measured volume of the liquid is introduced at *f*, and by applying suction at *a* it is drawn up the tube until the liquid has risen above the mark *c*. The liquid is now allowed to flow down the tube, and the time required for the meniscus to move from the mark *c*, to the lower mark *d*, is measured with a stop-watch. The experiment is now repeated with water, after which the viscosity of the liquid can be calculated by means of equation (43).

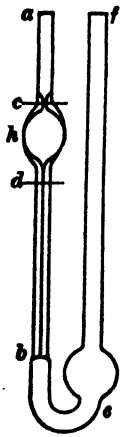

Fig. 23

The reciprocal of viscosity is called *fluidity*, i.e., $\phi = 1/\eta$. Fluidity may be regarded as a measure of the tendency of a liquid to flow, whereas viscosity is a measure of the resistance which a liquid offers to flowing.

The viscosity of liquids has been found to decrease about two per cent for each degree of rise in temperature. Increase of pressure, on the other hand, causes the viscosity of liquids to increase, the change in viscosity corresponding to equal increments of pressure being greater at high pressures than at low.

While there appears to be an abundance of experimental evidence to prove that the viscosity of a mixture of two or more liquids is not equal to the sum of the viscosities of the components, it is claimed by Bingham that there is both theoretical and experimental justification for the statement that fluidities are additive. He points out that the fluidity ϕ, of a mixture of two liquids whose fluidities are ϕ_1, and ϕ_2, respectively, may be represented by the equation

$$\phi = a\phi_1 + b\phi_2, \tag{44}$$

where a and b denote the volume concentrations of the two liquids. This equation has been found to hold in the case of liquids which are "inert," i.e., liquids which are not only individually non-associated but also exhibit no tendency to combine with each other.

Numerous applications of viscometric methods to various problems in both pure and applied chemistry might be cited. Thus, they have proven valuable in the study of such problems as keto-enol tautomerism, the determination of the order of chemical reactions, the existence of racemates in solution and the determination of transition points. In biology and medicine the viscometer has become an almost indispensable instrument for the study of the properties of blood and other animal fluids, while in the realm of technology it has been successfully applied to the solution of a wide variety of problems presented by the paint, rubber, glue, textile and other industries.

Plasticity. As has been pointed out in a previous paragraph, the law governing the flow of liquids through capillary tubes was discovered by Poiseuille and is expressed mathematically by equation (37). This equation may be re-arranged as follows: —

$$\text{Velocity of flow} = \frac{V}{t} = \left(\frac{\pi r^4}{8\eta l}\right)P. \tag{45}$$

From this expression it is apparent that the velocity of flow is proportional to the driving pressure. This type of flow is termed *viscous flow* and is to be differentiated from another type of flow exhibited by plastic solids, known as *plastic flow*.* Plastic flow differs from viscous flow in that an initial pressure P_0 is necessary to start it, whereas in the case of viscous flow no such initial impulse is required. The velocity of plastic flow is proportional to the difference between the normal driving pressure P and the initial starting pressure P_0. The distinction between viscous flow and plastic flow becomes clear when we compare the following equations expressing the velocity of the two types of flow: —

$$\text{Velocity of viscous flow} = \frac{V}{t} = k_v P, \tag{46}$$

$$\text{Velocity of plastic flow} = \frac{V}{t} = k_v(P - P_0). \tag{47}$$

For very high and very low values of $P - P_0$ the latter equation

* For further information on the subject of plastic flow the student is referred to the Journal of Physical Chemistry, 29, 1201–1282 (1925), where appear a series of papers of exceptional interest on this subject which were presented at the Plasticity Symposium held at Lafayette College, Oct. 17, 1924.

fails to hold, presumably because of slippage of the material through the viscometer. By substituting $P - P_0$ for P, in equation (45), the equation may also be applied to plastic flow. The analogue of fluidity, $1/\eta$, is known in the case of plastic flow as the *coefficient of mobility*, μ. The initial pressure P_0, known as the *yield-value*, has been found to be dependent upon the dimensions of the viscometer as well as upon the nature of the material. If the yield-value, P_0, be multiplied by the ratio of the radius, r, of the capillary tube to its length l, we obtain a quantity known as the *yield-value factor* which together with the mobility, μ, determines the plasticity of a given material. In fact, plasticity may be defined mathematically by the equation,

$$\text{Plasticity} = P_0 \frac{r}{l} \mu. \tag{48}$$

REFERENCES

Stoichiometry. Sydney Young.
The Viscosity of Liquids. Dunstan and Thole.
Fluidity and Plasticity. Bingham.

PROBLEMS

1. The critical temperature of ammonia is 130° C. and the critical pressure 115 atmospheres; calculate the values of the constants a and b in van der Waals' equation specifying the units. Plot the isotherms for 17° C., 130° C., and 160° C.

Ans. $a = 13895.8$, $b = 2.1155$ (units 1 gm., 1 cc., and 1 atm.).

2. For ether, $T_c = 193.8°$ C. and $p_c = 2706$ cm. of mercury. Evaluate the constants a and b for ether in van der Waal's equation and then calculate the value of the critical density.

Ans. $a = 3177.58$, $b = 1.818$ (units 1 gm., 1 cc., and 1 atm.); $d_c = 0.1834$ gm./cc.

3. The values of a and b for nitrogen are $a = 1660$, $b = 1.32$ respectively, referred to 1 gm., 1 cc., and 1 atm. Calculate the value of T_c, p_c, and v_c.

Ans. $T_c = -145.92°$; $p_c = 35.29$ atm.; $v_c = 3.96$ cc./gm.

4. The normal density of hydrogen is 0.089873 and that of oxygen is 1.42900. The coefficients of compressibility of the two gases are — 0.00054 and 0.000964 respectively. Calculate the atomic weight of hydrogen by the method of limiting densities assuming that the atomic weight of oxygen is 16.

5. The density of nitric oxide at 0° and 760 mm. is 1.3402; the critical temperature and the critical pressure are 179.5° abs. and 71.2 atmospheres respectively. Calculate the atomic weight of nitrogen by Berthelot's equation.

6. The ratio of the weight of 1 liter of methyl fluoride, CH_3F, to the pressure in atmospheres at three different pressures is as follows:

1.54507 at 760 mm.,
1.53576 at 506.67 mm.,
1.52665 at 253.33 mm.

Calculate the atomic weight of fluorine by the method of limiting densities.

7. Evaluate the constants for benzene in the vapor pressure formulæ of Dalton, Young and Kirchhoff-Rankine from the following experimental data:

10° 45.43 mm. 40° 181.08 mm. 70° 547.4 mm.

Compute the vapor pressure at 0°, 20°, 30°, 50°, 60°, 80°, 90°, and 100° by each of the above formulæ and compare the results with data given in the table on p. 73.

8. A volume of 50 liters of air in passing through a liquid at 22° C. causes the evaporation of 5 grams of substance, the molecular weight of which is 100. What is the vapor pressure of the liquid in grams per square centimeter? *Ans.* 25.

9. The critical temperature of normal pentane is 197°.15. The orthobaric densities of normal pentane in the liquid and vapor states at several temperatures are as follows:

Temp.	d_l	d_g
110°	0.5248	0.0203
130	0.4957	0.0310
150	0.4604	0.0476
180	0.3867	0.0935
190	0.3445	0.1269
195	0.3065	0.1609

From the foregoing data calculate the critical density of normal pentane.

10. Determine the critical temperature of ether by applying the law of the rectilinear diameter to the following experimental data, plotting densities against the corresponding values of temperature:

Temp.	172°.6	182°.2	187°.2	192°.3	194°.0	194°.5
Density	0.0952	0.1167	0.1389	0.1822	0.2231	0.2258
Temp.	194°.1	193°.5	190°.8	188°.9	187°.3	169°.3
Density	0.2843	0.3094	0.3593	0.3734	0.3844	0.4608

11. In a determination of the heat of vaporization of benzene with the Mathew's apparatus, the following experimental data were obtained: mass of benzene vaporized, 10.032 grams; duration of experiment, 8 min. 53.9 sec.; current strength, 1.000 ampere; resistance of heating coil, 7.4335 ohms; temperature, 79°.5 C. Calculate the heat of vaporization of benzene and also its molecular weight, assuming its boiling point to be 80.2° (760 mm.).

12. The boiling-point of ethyl propionate is 98°.7 C. and its heat of vaporization is 77.1 calories. Calculate its molecular weight.

13. The heat of vaporization of liquid ammonia at its boiling-point, under atmospheric pressure (−33°.5 C.) is 341 calories. Is liquid ammonia associated?

14. Calculate the surface tension of benzene in dynes per centimeter, the radius of the capillary tube being 0.01843 cm., the density of the liquid, 0.85, and the height to which it rises in the capillary, 3.213 cm.

Ans. 24.71 dynes/cm.

15. Find the molecular weight of benzene, the surface tension at 46° C. being 24.71 dynes per centimeter, its critical temperature, 288°.5 C., its density, 0.85 and the value of $k = 2.12$. *Ans.* 77.7.

16. At 14°.8 C. acetyl chloride (density = 1.124) ascends to a height of 3.28 cm. in a capillary tube the radius of which is 0.01425 cm. At 46°.2 C. in the same tube the elevation is 2.85 cm. and the density = 1.064. Calculate the critical temperature of acetyl chloride.

Ans. 234°.6.

17. From a certain tip the weights of a falling drop of benzene are 35.329 milligrams (temp. = 11°.4, density = 0.888) and 26.530 milligrams (temp. = 68°.5, density = 0.827). The molecular weight is the same in the liquid and gaseous states. Calculate the critical temperature of benzene. *Ans.* 286°.1.

CHAPTER IV

SOLIDS

General Properties of Solids. Solids differ from gases and liquids in possessing definite, individual forms. Matter in the solid state is capable of resisting considerable shearing and tensile stresses. In terms of the kinetic theory of matter, the mutual attractive forces exerted by the molecules of solids must be regarded as superior to the attractive forces between the molecules of gases and liquids. With one or two exceptions, all solids expand when heated, but there is no simple law expressing the relation between the increment of volume and the temperature. Rigidity is another characteristic property of solids, it being much more apparent in some than in others. Many solids are constantly undergoing a process of transformation into the gaseous state at their free surfaces, such a change being known as *sublimation.* Just as a gas, when sufficiently cooled, passes into the liquid state, so on cooling a liquid below a certain temperature, it passes into the solid state. The reverse transformations are also possible, a solid being liquefied when sufficiently heated, and the resulting liquid completely vaporized if the heating be continued. Heat energy is required to effect transition from the solid to the liquid state, just as heat energy is required to effect transition from the liquid to the gaseous state. Obviously a substance in the solid state contains less energy than it does in the liquid state. The number of calories required to melt 1 gram of a solid substance is called its *heat of fusion.*

It is often difficult to decide whether a substance should be classified as a solid or as a liquid. For example the behavior of certain amorphous substances, such as pitch, amber and glass, is similar to that of a very viscous, inelastic liquid. Solids are generally classified as *crystalline* or *amorphous.* In crystalline solids the atoms (sometimes molecules) are supposed to be arranged in some definite order, this arrangement manifesting itself in the crystal form. An amorphous solid on the other hand may be considered as a liquid possessing great viscosity and small

elasticity. The physical properties of amorphous solids have the same values in all directions, whereas in crystalline solids the values of these properties may be different in different directions. When an amorphous solid is heated, it gradually softens and eventually acquires the properties characteristic of a liquid, but during the process of heating there is no definite point of transition from the solid to the liquid state. On the other hand, when a crystalline solid is heated there is a sharp change from one state to the other at a definite temperature, this temperature being termed the *melting-point.*

Crystallography. The study of the definite geometrical forms assumed by crystalline solids is termed *crystallography.* The number of crystalline forms known is exceedingly large, but it is possible to reduce the many varieties to a few classes or systems by referring their principal elements — the planes — to definite lines called axes. These axes are so drawn within the crystal that the crystal surfaces are symmetrically arranged about them. This system of classification was proposed by Weiss in 1809. He showed that, notwithstanding the multiplicity of crystal forms encountered in nature, it is possible to consider them as belonging to one of six systems of crystallization.

The six systems of Weiss are as follows: —

1. *The Regular System.* Three axes of equal length, intersecting each other at right angles (Fig. 24).

2. *The Tetragonal System.* Two axes of equal length and the third axis either longer or shorter, all three axes intersecting at right angles (Fig. 25).

3. *The Hexagonal System.* Three axes of equal length, all in the same plane and intersecting at angles of 60°, and a fourth axis, either longer or shorter and perpendicular to the plane of the other three (Fig. 26).

4. *The Rhombic System.* Three axes of unequal length, all intersecting each other at right angles (Fig. 27).

5. *The Monoclinic System.* Three axes of unequal length, two of which intersect at right angles, while the third axis is perpendicular to one and not to the other (Fig. 28).

6. *The Triclinic System.* Three axes of unequal length no two of which intersect at right angles (Fig. 29).

The position of a plane in space is determined by three points in a system of coördinates, and consequently the position of the

face of a crystal is likewise determined by its points of intersection with the three axes, or by the distances from the origin of the system of coördinates at which the plane of the crystal face intersects the three axes.

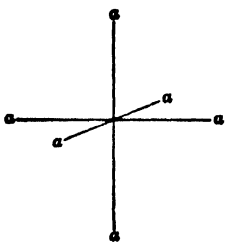

Fig. 24

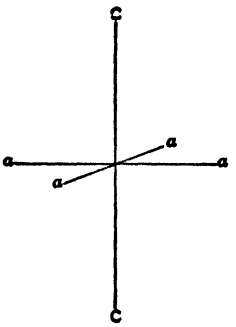

Fig. 25

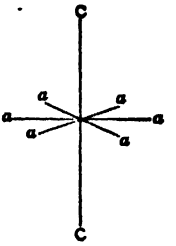

Fig. 26

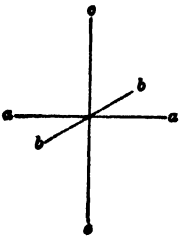

Fig. 27

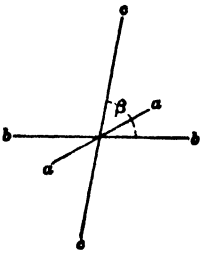

Fig. 28

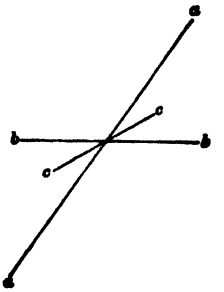

Fig. 29

Crystal Notation. As has already been pointed out, it is convenient in the geometrical description of a crystal to refer the position of its facial planes to a set of imaginary axes within the crystal, the so-called *crystallographic axes*. These axes are so chosen as to permit the precise description of the faces of the crystal in the simplest possible manner. In Fig. 30, let AOA', BOB' and COC', representing the three crystallographic axes, be designated as the a-, b-, and c-axes, respectively. The length and mutual inclination of these axes determine the form of the crystal. The angles between the axes, known as the *axial angles*, are symbolized as follows: — the angle $BOC = \alpha$, the angle $COA = \beta$ and the angle $AOB = \gamma$. The axial angles together with the axial ratios, $a : b : c$, are characteristic for each individual crys-

talline substance and are collectively known as the *crystallographic constants* of the substance. The crystallographic axes can be prolonged in either direction from the origin O, one direction being arbitrarily designated as positive and the opposite direction negative. The negative direction is indicated by a horizontal line placed over the letters representing the axes.

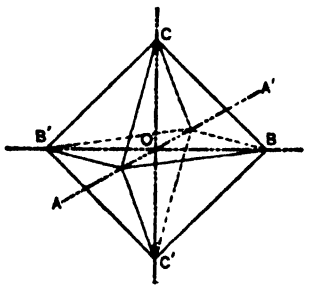

Fig. 30

On the axes $AO\overline{A}$, $BO\overline{B}$ and $CO\overline{C}$ let the lengths $(a, \bar{a})$, $(b, \bar{b})$ and $(c, \bar{c})$ respectively be laid off, and let a set of planes be drawn in such positions that they intersect the $AO\overline{A}$ axis at the distance a, the $CO\overline{C}$ axis at $\bar{c}$, the $BO\overline{B}$ axis at b, etc. The lengths a, b, c and $\bar{a}$, $\bar{b}$, $\bar{c}$ are termed *parameters*. The plane ABC having the parameters a, b, c is known as the abc plane; the plane ABC' is known as the $ab\bar{c}$ plane; the plane $AB'C'$ is known as the $a\bar{b}\bar{c}$ plane, etc. The exact position of the faces becomes fixed when the directions of the a-, b- and c-axes and the parameters a, b and c are determined. For example, if a plane be so drawn as to cut the a-axis at $a/2$, the b-axis at $b/3$ and the c-axis at $c/4$, then the fractional intercepts $a/2$, $b/3$ and $c/4$ determine the position of the plane. This notation is awkward because of the fractional values of the intercepts and for this reason it is customary to employ their reciprocals, viz., 2, 3, 4, the plane being described as the 234-plane. Similarly, the plane abc, Fig. 30, is the 111-plane. These numbers are known as *indices*, and conventionally the indices are always given in the order of the a-, b- and c-axes, respectively. As the slope of the crystal faces becomes more acute, the value of the parameters becomes correspondingly smaller until in the limiting case, the plane ∞a, ∞b, c, denoted by the indices 001, is parallel to the axes in question. Since the three indices of a crystal face may be multiplied or divided by any desired factor without altering their relative values, it is customary to reduce the ratios to their lowest terms. This system, devised in 1829 by W. H. Miller, has been received with greater favor than any of the other numerous systems of crystal notation which have been proposed.

Steno's Law. The fundamental law of crystallography, discovered by Steno in 1669, may be stated thus: — *The angle between*

two given crystal faces is always the same for the same substance. The fact that every crystalline substance is characterized by a constant interfacial angle, affords a valuable means of identification which is used by both chemists and mineralogists. The instrument employed for the measurement of the interfacial angles of crystals is called a *goniometer.* The crystal to be measured is mounted at the center of the graduated circular table of the goniometer, and the image of an illuminated slit, reflected from one surface of the crystal, is brought into coincidence with the cross-wires in the eye-piece of the telescope. The table is then turned until the image of the slit, reflected from the adjacent face of the crystal, coincides with the cross-wires. The interfacial angle of the crystal is determined by the number of degrees through which the table has been turned.

Properties of Crystals. The properties of all crystals, except those belonging to the regular system, exhibit differences dependent upon the direction in which the particular measurements are made. Thus the elasticity, the thermal and electrical conductivities, and in fact all of the physical properties of crystals which do not belong to the regular system, have different values in different directions. Crystals whose physical properties have the same values in all directions are termed *isotropic,* while those in which the values are dependent upon the direction in which the measurements are made, are called *anisotropic.* Certain amorphous substances, such as glass, which are normally isotropic, may become anisotropic when subjected to tension or compression. The phenomenon of double refraction observed in all crystals, except those belonging to the regular system, is due to their anisotropic character. Crystals belonging to the tetragonal and hexagonal systems resemble each other in one respect, viz.: that in all of them there is one direction, called the optic axis (coincident with the principal crystallographic axis), along which a ray of light is singly refracted, while in all other directions it is doubly refracted. In crystals belonging to the rhombic, monoclinic, and triclinic systems, there are always two directions along which a ray of light is singly refracted. A crystal of Iceland spar ($CaCO_3$) affords a beautiful illustration of double refraction. On placing a rhomb of this substance over a piece of white paper on which there is an ink spot, two spots will be seen. On turning the crystal, one spot will remain stationary while the other spot will

revolve about it. This property of Iceland spar is utilized in the construction of Nicol prisms for polariscopes.

The examination of sections of anisotropic crystals in a polariscope between crossed Nicol prisms, reveals something as to their crystal form. As has been stated, crystals of the tetragonal and hexagonal systems are *uniaxial*. If a section is cut from such a crystal perpendicular to the optic axis, and this is placed between the crossed Nicol prisms of a polariscope, in a convergent beam of white light, a dark cross and concentric, spectral-colored circles will be observed, Fig. 31. Upon turning the analyzer through 90° the colors of the circles will change to the respective complementary colors and the dark cross will become light. Crystals of the rhombic, monoclinic, and triclinic systems are *biaxial*. If a section of a biaxial crystal, cut perpendicular to the line bisecting the angle between the two axes, be placed in the polariscope and examined as in the preceding case, a series of concentric spectral-colored lemniscates surrounding two dark centers and

Fig. 31

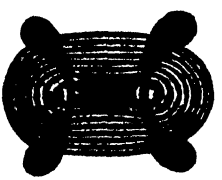

Fig. 32

pierced by dark, hyperbolic brushes, will be observed, as shown in Fig. 32. On rotating the analyzer, the colors will change to the corresponding complementary colors, as in the case of uniaxial crystals. The appearance of these figures is so varied and characteristic as to furnish, in many cases, a very satisfactory means of identifying anisotropic crystals.

Etch Figures. The solubility of crystals has been shown to be different in different directions. Thus, if the surface of a crystalline substance be highly polished and then treated for a short time with a suitable solvent, faint patterns, known as *etch figures*, will appear as a result of the inequality of the rate of solution in different directions. When these figures are examined under the microscope the crystal-form can generally be determined. The examination of etch figures has come to be of prime importance to the metallographer. Thus, when an appropriate solvent is

applied to the polished surface of an alloy, not only is the crystal form revealed by the etch figures, but also the presence of various chemical compounds may be recognized. By a careful study of the etch figures developed on the surface of highly polished steel, the metallographer may gather important information as to its previous history, especially its heat treatment.

Crystal Form and Chemical Composition. From the preceding paragraphs it might be inferred that the same substance always assumes the same crystal form. While this is true in general, there are some substances which appear in several different crystal forms. This phenomenon is termed *polymorphism.*

Calcium carbonate is an example of a substance crystallizing in more than one form. As calcite, it crystallizes in the hexagonal system, while as aragonite, it crystallizes in the rhombic system. Such a substance is said to be *dimorphous.* Of the several factors controlling polymorphism, temperature is the most important. Thus sulphur crystallizes at temperatures above 95°.6 in the monoclinic system, while at lower temperatures it assumes the rhombic form. The temperature at which it changes from one form into the other is termed its *transition temperature.* As has been mentioned in an earlier chapter (p. 13), some substances may crystallize in the same form, the characteristic interfacial angles being nearly identical. Such substances are said to be *isomorphous.* This phenomenon, discovered by Mitscherlich, has been of great use in connection with the earlier investigations on atomic weights, as has already been pointed out.

There can be little doubt as to the existence of an intimate connection between crystalline form and chemical composition. Ever since the early part of the nineteenth century, when Haüy established the science of crystallography, various attempts have been made by chemists and crystallographers to connect crystalline form with chemical constitution. In 1906, Barlow and Pope* made a most notable contribution to the theories concerning the relation between crystalline form and chemical constitution. Their ideas may be summarized as follows: — If each atom be considered as appropriating a certain space, called its sphere of atomic influence, then (1) *the spheres of atomic influence are so arranged as to occupy the smallest possible volume in every crystal;* (2) *the volumes of the spheres of atomic influence in any substance*

* Jour. Chem. Soc., 91, 1150 (1907).

are proportional to the valences of the constituent atoms; (3) the volumes of the spheres of influence of the atoms of different elements of the same valence are nearly equal, any variation being in harmony with their relations in the periodic system.

Compressibilities of the Solid Elements. A series of careful measurements of the compressibilities of the elements by T. W. Richards and his collaborators,* has revealed the fact that compressibility is a periodic function of atomic weight. Richards has advanced some interesting suggestions as to the importance of compressibility in connection with intermolecular cohesion and atomic volume. In fact, Richards' theory of compressible atoms may be regarded as a valuable supplement to the theory of Barlow and Pope and, taken together, these two theories constitute a rational basis for the science of chemical crystallography.

X-Rays and Crystal Structure. Much light has recently been shed upon the question of the arrangement of the atoms and molecules within crystals by the interesting investigations which have been carried out on the transmission and reflection of X-rays by crystalline substances. It is now a well-established fact that X-rays are in reality light waves of extremely short wave-length. The wave-length of the X-ray is approximately 1×10^{-8} cm. or, in other words, the wave-length of the X-ray is of the same order of magnitude as the distance between contiguous atoms in crystals.

In 1912, Laue pointed out that the regularly arranged atoms of a crystal should act as a three-dimensional diffraction grating toward X-rays. He showed mathematically that on traversing a thin section of a crystal, a pencil of X-rays should give rise to a diffraction pattern arranged symmetrically round the primary beam as a center. A photographic plate placed perpendicular to the path of the rays and behind the crystal should reveal, on development, a central spot due to the action of the primary rays, and a series of symmetrically grouped spots due to the diffracted rays.

Laue's predictions were verified experimentally by Friedrich and Knipping,† who obtained numerous plates showing a variety of geometrical patterns corresponding to the structural differences of the crystals examined. In Figs. 33*a* and 33*b*, Laue photographs of magnesium oxide and diopside, respectively, are shown.

* Zeit. phys. Chem., 61, 77, 100, 171, 183 (1908).

† Ann. d. Phys., 41, 971 (1913).

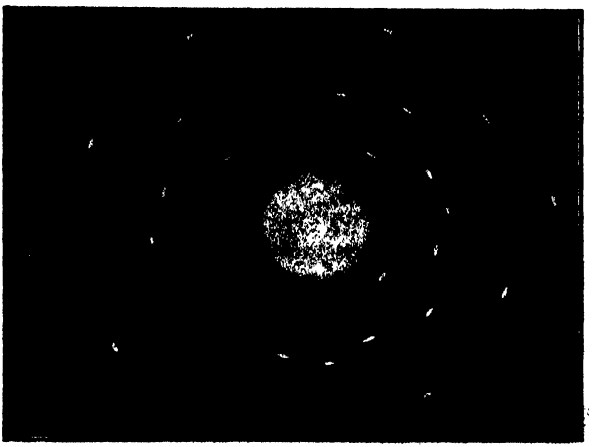

Fig. 33*a*

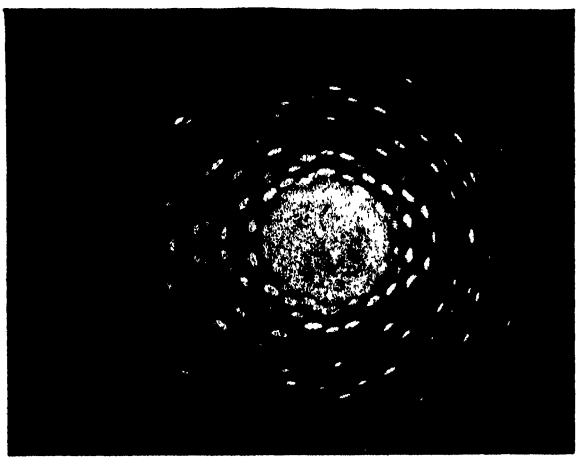

Fig. 33*b*

The analysis of the Laue diffraction patterns, while furnishing valuable information as to the internal structure of crystals, is nevertheless extremely complex. In addition to the original method of Laue for the investigation of crystal structure, two

other methods have been developed which have proven to be of great value.

Before entering upon a discussion of these methods, however, it may clarify the student's understanding of the subject if we digress to consider very briefly the possible geometrical arrangements of the structural units constituting a simple crystal.

The Structure of a Cubical Crystal. Among the first crystalline substances studied by the method of X-ray analysis was sodium chloride, a compound which crystallizes in the cubic system. In the cubic system there are three possible arrangements or *space-lattices* of the fundamental structural units. These are known as the *simple cubic*, the *face-centered cubic* and the *body-centered cubic* lattices. It is convenient to regard the entire space-lattice as made up of an aggregation of cells among which the structural units of the macroscopic crystal are distributed. The three types of cells characteristic of the three cubic lattices are shown diagrammatically in Fig. 34. It will be observed that in the simple cubic

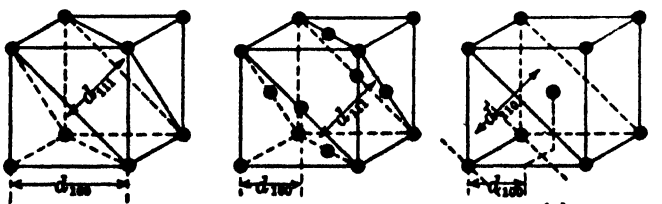

Fig. 34

lattice, a single structural unit is situated at each corner of the cubic cell. In the face-centered lattice, there is one unit situated at each corner of the cubic cell and also one unit in the center of each face. In the body-centered lattice, there is one unit at each corner and also one unit at the center of the cubic cell. The relative spacing of the planes containing these units in planes drawn (1) parallel to the cube face, (2) perpendicular to the face diagonal and (3) perpendicular to the cube diagonal may be readily calculated for each of the three types of space lattice. These planes correspond with possible faces of the crystal and their respective positions, as defined in terms of Miller's indices, are (100), (110) and (111). In Fig. 34*a* and Fig. 34*b*, the intersecting planes correspond with the (111)-planes, whereas in Fig. 34c they

correspond with the (110)-planes. These three sets of planes constitute the principal planes in each type of lattice. From the geometry of these groupings it may easily be proven that the following ratios represent the three types of lattice, the (100)-planes being taken as unity: —

Simple cubic, $d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}}$

Face-centered cubic, $d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$

Body-centered cubic, $d_{100} : d_{110} : d_{111} = 1 : \sqrt{2} : \frac{1}{\sqrt{3}}$

The Bragg Method of X-Ray Analysis. W. H. Bragg and his son, W. L. Bragg,* showed that the diffraction of X-rays by the atoms of a crystal can be studied much more simply by employing the crystal as a reflection grating, rather than as a transmission grating, as in the method of Laue. The reflection of X-rays from the face of a crystal may be likened to the reflection of a beam of light from a bundle of thin glass plates of equal thickness. It is known that reflection from a bundle of plates will take place only at definite angles, the values of which will be dependent upon the wave-length of the incident light, as well as upon the thickness of the plates. The plates of glass correspond to the planes of atoms within the crystal, for the space-lattice arrangement of the structural units, or atoms, of a crystal is such that they are to be considered as lying in parallel planes, the orientation of which is determined by their indices and by the symmetry of the crystal. Each crystal face is developed parallel to one of these planes, the development favoring, as a general rule, those planes containing the maximum number of atoms.

The Braggs pointed out that it was not only possible but far simpler to consider the diffraction of X-rays by a crystal as reflections from these successive planes of atoms rather than as diffractions from a tri-dimensional grating in which the atoms act as diffracting centers. In other words, when a beam of "monochromatic" X-rays is incident upon the face of a crystal the rays undergo "reflection" in a manner similar to the reflection of mono-chromatic light from a bundle of parallel glass plates.

* "X-Rays and Crystal Structure."

Let AA', BB', CC', etc., in Fig. 35, represent a series of planes of atoms parallel to some face of a crystal and separated from each other by a distance d. Let a beam of mono-chromatic X-rays of wave-length λ fall upon the plane AA'. The atoms in this face at once become centers of vibration and emit wavelets in all directions. In one particular direction, R, however, the wavelets scattered by the numerous atoms in the plane AA' will be in like phase and consequently will reinforce each other. The direction of the reflected beam is such that the angles of incidence and reflection are equal. The wavelets sent out in other directions by the atoms in the plane AA' neutralize each other by mutual interference. Owing to the penetrating character of X-rays relatively little energy is lost by reflection at AA' and the incident radiation enters the crystal passing through the successive planes of atoms BB', CC', etc. At each of these planes a portion of the incident radiation suffers reflection in a manner entirely similar to that occurring at AA', the direction of the reflected radiation being in each case the same. Obviously the wavelets reflected from the successive planes will reinforce each other only when they meet in like phase. It may readily be shown that this condition is fufilled by the equation,

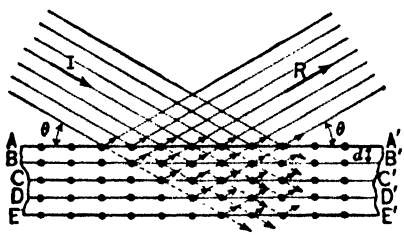

Fig. 35

$$n\lambda = 2\,d \sin \theta, \qquad (1)$$

where λ denotes the wave-length of the incident radiation, n the order of reflection, d the distance between the successive planes and θ the angle of reflection. It follows that only one particular wave-length will be reflected in the direction R with sufficient intensity to be detected, the other wave-lengths being neutralized through interference between the wavelets reflected from the different planes. It should be pointed out that the reflection of X-rays differs from the reflection of visible radiation in two respects: — first, the reflection of X-rays is not wholly a surface phenomenon; and second, only a single wave-length is reflected at each angle of incidence. Consequently, if X-rays are incident

upon the face of a crystal for which d is known, the value of λ for the radiation used may be determined by measuring the angles at which the reflections occur. On the other hand, if the wave-length of the incident radiation is known, it becomes possible to determine the spacing of the atomic planes within the crystal. The former enables us to investigate the structure of atoms, as will be shown in a subsequent chapter, while the latter provides us with the means of determining the arrangement of the atoms in crystals.

In order to study the reflection of X-rays from the faces of crystals, the Braggs devised an instrument known as the X-ray spectrometer, Fig. 36. In this instrument, a beam of X-rays, preferably of a single wave-length, is rendered parallel by means of two narrow slits A and B; after passing through these slits, the rays are reflected from one of the faces of a crystal C, which is mounted as a reflection grating upon the table of the spectrometer, and the reflected beam then enters the so-called " ionization chamber " where the intensity of the beam is measured.

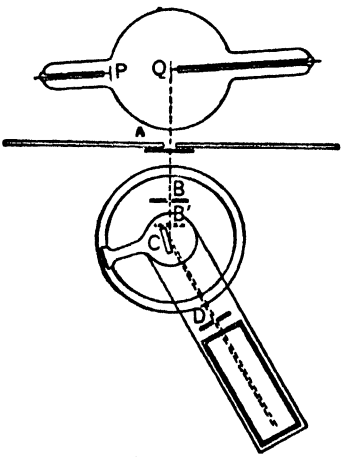

Fig. 36

The ionization chamber, which is filled with some easily ionizable gas, such as sulphur dioxide, is connected with an electroscope by means of which the intensity of the ionization produced by the reflected X-rays can be measured. The crystal and the ionization chamber are rotated about a common axis, the face of the crystal and the ionization chamber being maintained at the same angle as that between the face of the crystal and the incident beam. The intensity of the ionization corresponding to successive settings of the crystal is measured and from these readings the angles corresponding to the maximum reflections are determined. The positions of the maximum reflections from the (100), (110) and (111) faces of a crystal of sodium chloride, obtained with an X-ray tube having a palladium anti-cathode, are shown in Fig. 37. The ordinates represent intensities of ionization as measured by the electrometer. The first order reflections for

the (100), (110) and (111) planes are found to occur at 5.9°, 8.4° and 5.2° respectively.

If the equation,

$$n\lambda = 2\,d \sin\theta,$$

be rearranged in the form,

$$\sin\theta = \frac{n\lambda}{2\,d},$$

it is apparent that, for a particular source of X-rays and for a particular crystal plane, λ and d will remain constant and the

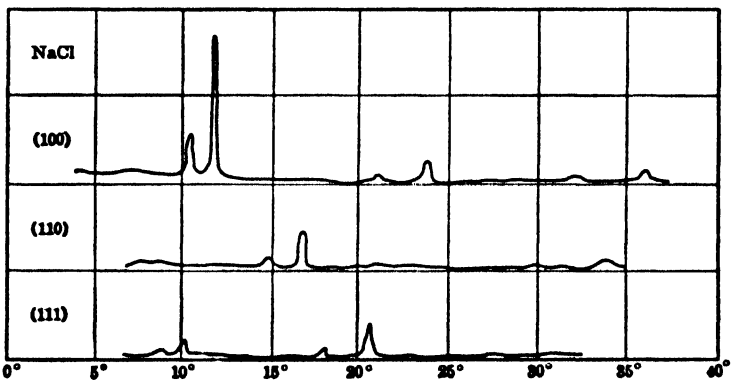

Fig. 37

Abscissa = angle of setting of ionization chamber = 2θ.

ratio of successive values of sin θ should reduce to small whole numbers corresponding to the order of reflection n. For example, employing an X-ray tube with a palladium anti-cathode and a crystal of sodium chloride, maximum reflections were obtained at the following angles: $\theta = 5.9°$, $\theta = 11.85°$ and $\theta = 18.15°$. The ratio of the sines of these angles is 0.103 : 0.205 : 0.312, or very nearly 1 : 2 : 3, as was to be expected. From each of these angles, the interplanar distance d can be calculated. Thus,

$$d = \frac{n\lambda}{2 \sin\theta} = \frac{2\,\lambda}{2 \times 0.205} = 4.88\,\lambda.$$

Returning to the experimental data of Fig. 37, and taking the ratio of the sines of the angles corresponding to the first order

reflections from the three planes, (100), (110) and (111), we have: $\sin 5°.9 : \sin 8°.4 : \sin 5°.2 = 0.103 : 0.146 : 0.094 = 1 : 1.42 : 0.91$, and since

$$d = \frac{n\lambda}{2 \sin \theta},$$

it follows that the corresponding values of d should be in the ratios of the reciprocals of these numbers, i.e.,

$$d_{100} : d_{110} : d_{111} = \frac{1}{1} : \frac{1}{1.42} : \frac{1}{0.91} = 1 : 0.71 : 1.10.$$

But we have already seen that, for a face-centered cubical crystal,

$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.71 : 1.15,$$

and therefore, the fundamental space-lattice of a crystal of sodium chloride is face-centered.

If the structural unit in a crystal of sodium chloride is the molecule, NaCl, the chlorine atoms may be assumed to be so distributed that their centers coincide with the points of the fundamental space-lattice. In like manner, the centers of the sodium atoms may be thought of as coinciding with a second lattice, identical with the first but slightly displaced from it. Since the fundamental lattice in a crystal of sodium chloride has been shown to be face-centered, the problem presents itself of determining the orientation of the lattice containing the chlorine atoms relative to that containing the sodium atoms. Since the efficiency of an atom as a reflector of X-rays is proportional to its atomic weight, it follows that the relative positions of the atoms in the crystal should be revealed by the relative intensities of the reflected rays. The chlorine atoms being one and one-half times as heavy as the sodium atoms, it is reasonable to assume that the reflections due to the chlorine lattice will be predominant, and that the reflections due to the sodium lattice will be comparatively weak. If we further assume the sodium lattice to be displaced from the fundamental chlorine lattice by one-half the length of the side of the cube, an alternate arrangement of the sodium and chlorine atoms along each edge of the cube will result. Such an arrangement is shown in Fig. 38. In this arrangement, the planes parallel to the faces of the cube contain an equal number of both kinds of atoms and the spacing of the planes corresponds to that of the fundamental face-centered lattice. The same statement applies to the

planes parallel to the (110) faces. In the case of the (111) faces, however, the foregoing arrangement brings the planes containing the sodium atoms midway between the (111) faces of the fundamental lattice. The influence of these planes on the reflections from the (111) faces can be easily predicted. If the difference in path between waves reflected from two contiguous chlorine planes is equal to one wave-length, obviously the difference in path between waves reflected from the chlorine planes and the intermediate sodium plane will be one-half wave-length, and, therefore, there will be total interference. That is, if the intensity of reflection from the sodium plane were exactly equal to that from the chlorine planes, the reflected rays would completely neutralize each other. On the other hand, if the intensity of the reflection from the sodium plane is less than the intensity of the reflections from the chlorine planes, a relatively weak resultant reflection will be obtained. That this is exactly what occurs may be seen by inspecting the curve of intensities of reflected rays from the (111) plane in Fig. 37. The experimental data, therefore, afford a very beautiful confirmation of the theoretical predictions as to the ultimate structure of crystals of sodium chloride.

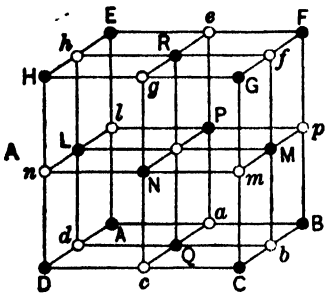

Fig. 38

Calculation of Wave-lengths of X-Rays. If the arrangement of the atoms in a crystal of sodium chloride be such as is indicated in Fig. 38, it is a relatively simple matter to compute, not only the interplanar distance d, but also the wave-length of the X-rays employed to establish its crystalline structure.

As will be seen from Fig. 38, in each elementary cubic cell there is one chlorine atom at each corner and also one chlorine atom at the center of each face. Furthermore, since each one of the corner atoms is common to eight other similar adjacent cubic cells, only one-eighth of its mass can be considered as belonging to any one of the eight cells. In like manner, each face-centered atom is common to two adjacent cubes and hence contributes only one-half of its mass to each of the two cubes. Therefore, the eight corner atoms contribute the mass of one atom, and the six center

atoms contribute the mass of three atoms, to a single cubic cell. In other words, the total mass of chlorine associated with a single cubic cell is equal to the mass of only four chlorine atoms. In precisely the same way, it may be shown that the mass of four sodium atoms is also associated with a single cubic cell, and each cell may be considered as having a mass equal to that of four molecules of sodium chloride. The specific volume of sodium chloride being 27.0 cc., it follows that the volume associated with four molecules, or the volume of a single cubic cell, will be

$$4 \times 27.0/6.06 \times 10^{23} = 178 \times 10^{-24} \text{ cc.},$$

where 6.06×10^{23} is Avogadro's constant, i.e., the actual number of molecules in one gram-molecule of sodium chloride. The length of the edge of the cell is determined by extracting the cube root of 178×10^{-24}, $= 5.62 \times 10^{-8}$ cm. The distance between the planes parallel to the (100) face, d_{100}, will be one-half of this number, or 2.81×10^{-8} cm.

Having determined the value of d_{100} and having previously found that $d_{100} = 4.88\ \lambda$ for X-rays from a palladium anticathode, it follows that

$$\lambda = 2.81 \times 10^{-8}/4.88 = 0.56 \times 10^{-8} \text{ cm.}$$

It is possible, therefore, to determine the wave-length of X-rays by means of a crystal of known structure in precisely the same manner as in the determination of wave-lengths of light by means of a diffraction grating.

The Hull, Debye-Scherrer Method of X-Ray Analysis. A serious disadvantage inherent in the Bragg method of X-ray analysis is the fact that well-developed and comparatively large crystals are required. Another method of investigating crystal structure in which the substance is studied in the form of powder was devised almost simultaneously by A. W. Hull* in this country and Debye and Scherrer† in Germany.

If a parallel beam of mono-chromatic X-rays is allowed to pass through a finely divided crystalline substance, a characteristic spectrum, made up of fine lines, will be produced upon a properly placed photographic film. These lines correspond to the reflections from the different faces of the minute crystalline particles of the

* Phys. Rev., 10, 661 (1917); Jour. Am. Chem. Soc., 41, 1168 (1918).

† Physikal: Zeit., 17, 277 (1916); 18, 291 (1917).

powdered substance. Not only does the method of powders furnish essentially the same information as that supplied by the spectrometric method but it does so in a single experiment, whereas, with the spectrometric method, there must be as many separate experiments as there are crystal faces. Furthermore, it has the advantage over the preceding methods that, instead of a well developed crystal of appreciable size, merely a very small amount of crystalline powder is all that is required; in fact, Hull has found that the amount of material necessary for a complete determination of crystal structure need not be more than one cubic millimeter. In the diagram of Hull's apparatus, shown in Fig. 39, T'

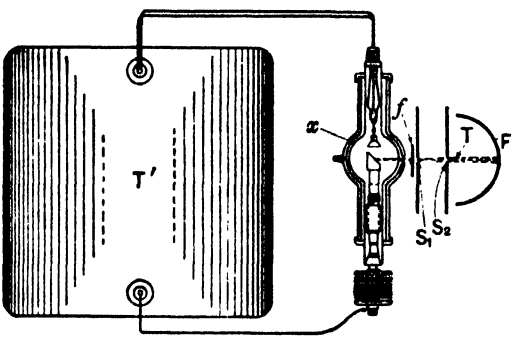

Fig. 39

is a transformer for operating the Coolidge X-ray tube, x; f is a sheet of metal, serving as a filter; S_1 and S_2 are slits in thin sheets of lead; T is a thin-walled tube, about one mm. in diameter, containing the powdered crystal; F is a narrow strip of photographic film bent over a semi-circular strip of brass, concentric with T. A typical spectrogram is reproduced in Fig. 40.

This method has proven of particular value to the metallographer in determining the crystalline structure of metals and alloys. If, for example, the powder under examination consists of a very large number of minute cubical crystals orientated in all possible directions, some of the crystals will be so placed as to reflect rays from their (100) planes, others from their (110) planes and still others from their (111) planes. But in each case the reflection will take place at a definite angle and will give rise to a series of lines on the film corresponding to the reflection maxima for each set of planes. Of course there will be several sets of such

lines depending upon the order of reflection. To facilitate the work of the experimenter, a scale is provided which gives directly the spacing, — divided by the order of reflection, — due to any line on the film when the shadow cast by the powder is placed opposite the zero reading of the scale.

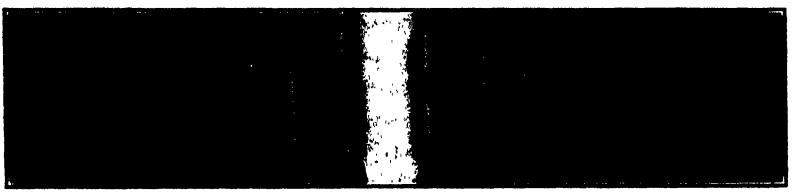

Fig. 40

While it is a comparatively easy task to determine the orientation of the atoms in a cubical crystal in which the atoms are all alike, it becomes increasingly difficult to establish the structure of crystals of lower degrees of symmetry and of compounds in which several kinds of atoms are present. Charts have been devised by Hull and Davey whereby the orientation of the atoms in crystals belonging to the cubic, hexagonal and tetragonal systems may be easily determined. In the case of compounds, it has been found that the heavier atoms reflect the most energy, and, in consequence, the variations in intensity of the lines on the film are significant in the X-ray analysis of compounds.

The powder method has been applied by Hull to the chemical analysis of mixtures of salts. For example, chemical analysis may reveal the presence of sodium, potassium, chlorine and bromine in a given sample and it is necessary to know whether sodium chloride and potassium bromide or potassium chloride and sodium bromide or all four salts are present in the mixture. Although this question cannot be answered by ordinary chemical analysis, Hull has shown that the powder method of X-ray analysis offers an easy solution of the problem. An X-ray photograph of the mixed crystalline powder furnishes a set of lines from which it is possible to determine the composition of the mixture by comparison with similar photographs made with the pure salts alone. Furthermore, by studying the relative intensities of the lines it is even possible to estimate roughly the amounts of each salt present in the mixture.

Heat Capacity of Solids. Recent investigations of specific heats of solids at extremely low temperatures have resulted in the formulation of several interesting relationships between heat capacity and temperature.

At ordinary temperatures the molecules of a crystalline solid may be assumed to be in a state of violent motion. As the temperature is lowered the amplitude of the molecular oscillations steadily diminishes, until finally at the absolute zero, there is in all probability a complete cessation of motion. In the neighborhood of the absolute zero, where the amplitude of the molecular oscillations is negligible, a crystalline solid may be assumed to possess the properties characteristic of a perfectly elastic body. In other words, the crystalline forces holding the molecules together would preponderate over the feeble thermal forces tending to initiate molecular oscillations within the solid. Under these conditions the solid as a whole would exhibit the same behavior as a single molecule, that is to say, the solid would function as a perfectly elastic body.

On this assumption Debye* has derived the following equation expressing the heat capacity of a solid, C_v, in terms of its absolute temperature, T,

$$C_v = 71.9 \frac{T^3}{\theta^3}. \tag{2}$$

In this equation θ is a constant characteristic of each solid and has the same dimensions as T. The value of θ varies between the limits $\theta = 50$ for calcium and $\theta = 1840$ for carbon. The agreement between the observed and calculated values of C_v has been found to be excellent up to $T = \theta/12$.

When this latter temperature is exceeded, the molecules of the solid begin to absorb more and more heat energy and to vibrate independently about their centers of oscillation. The failure of Debye's equation is to be expected under these conditions since the solid is no longer behaving as one large molecule. Obviously the lighter the molecules and the greater the crystalline forces within the solid, the higher must the temperature become before the individual molecules can acquire appreciable kinetic energy. This is apparent from the familiar dynamical principle, that the kinetic energy of a vibrating particle is proportional to its mass

* Ann. Physik., 39, 789 (1912).

and to the square of its vibration frequency. In the case of lead, which is a soft, malleable solid with a relatively low melting-point, it is reasonable to infer that the crystalline forces are feeble, and consequently we should expect that molecular and atomic vibrations would be set up at quite low temperatures. Furthermore, since the atoms of lead are extremely heavy, their kinetic energy must be great. The correctness of these conclusions is confirmed by the fact that the Debye equation when applied to lead has been found to hold only over a very short range of temperature. On the other hand, the equation has been found to hold for the diamond up to a temperature of about 200° absolute. In this case we have a solid in which the crystalline forces are extremely powerful and in which the atoms are relatively light. A fairly high temperature must be attained before the energy absorbed by the individual atoms of the diamond acquires appreciable magnitude.

The absorption of energy by the vibrating molecules continues to increase as the temperature is raised until ultimately, at the melting-point of the solid, the crystalline forces become negligible. As this temperature is approached, therefore, the intermolecular restraint becomes less and less and the mean kinetic energy of the molecules approaches that of the molecules of the molten solid.

As has already been stated in Chapter I (p. 10), Dulong and Petit, in 1819, discovered the interesting fact that the atomic heats of the solid elements have a constant value of 6.4. The importance of this generalization in connection with the verification of atomic weights has already been pointed out. Lewis* has directed attention to the fact that it is much more rational to calculate the atomic heat of an element from the specific heat at constant volume rather than from the specific heat at constant pressure. While it is impossible to measure the specific heat at constant volume, its value may be derived from the specific heat at constant pressure by an application of the laws of thermodynamics. Thus, Lewis has obtained the formula

$$C_p - C_v = \frac{T\alpha^2 V}{41.78\,\beta}, \qquad (3)$$

where T denotes the absolute temperature, α the coefficient of expansion, β the coefficient of compressibility, C_p and C_v the atomic

* Jour. Am. Chem. Soc., 29, 1165 (1907).

specific heats at constant pressure and constant volume respectively and V the atomic volume. By means of this equation, Lewis has established the following generalization: *Within the limits of experimental error, the atomic heat at constant volume, at* 20° C., *is the same for all solid elements whose atomic weights are greater than that of potassium, and is equal to* 5.9. In the case of a solid having a high melting-point, the violent agitation of its constituent molecules and atoms, as the temperature is raised, will undoubtedly produce a corresponding increase in the amplitude of vibration of its electrons together with an increase in their translational velocity among the molecules. Under these conditions, the specific heat at constant volume should be greater than 5.9

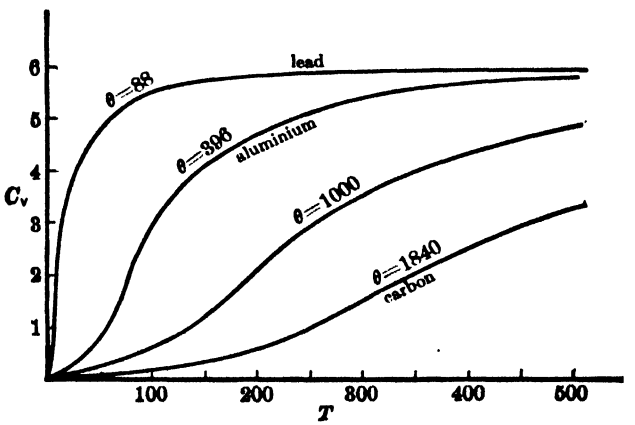

Fig. 40*a*

calories. This conclusion cannot be verified experimentally until the values of α and β in the foregoing equation have been determined at high temperatures.

The complete heat capacity curves for three typical solid elements, lead, aluminium, and carbon, are given in Fig. 40*a*. It is apparent from these curves that the absorption of heat energy by a crystalline solid may be considered as taking place in three distinct stages, as follows: — (1) In the neighborhood of the absolute zero, the heat capacity remains practically zero; (2) the heat capacity increases rapidly with the temperature; and (3) the heat capacity increases slowly, approaching asymptotically the limiting value 5.9 for $T = \infty$. For a malleable, low melting element of

high atomic weight, such as lead, the first two stages are very short and the final stage commences at a low temperature. On the contrary, with a hard, high melting element of low atomic weight, such as carbon in the form of diamond, the final stage is not reached at any temperature within the range covered by the experiments.

Liquid Crystals. In addition to possessing well-defined geometrical forms, crystalline substances are characterized by their resistance to deformation when subjected to mechanical stress, and by the property of melting sharply at definite temperatures with the production of transparent liquids.

In 1888, two substances, cholesteryl acetate and cholesteryl benzoate, were found by Reinitzer* to behave in an anomalous manner when heated. At definite temperatures these substances melted to turbid liquids which, in turn, became clear on further heating, the latter change also taking place at definite temperatures. On cooling the clear liquids, the reverse series of changes was found to occur.

Examination of the turbid liquids revealed the fact that they resembled ordinary liquids in their general behavior, such as assuming the spherical shape when suspended in a medium of the same density, or of rising in a capillary tube under the influence of surface tension. But in addition to possessing the properties characteristic of the liquid state, Lehmann discovered that they possessed optical properties which had hitherto been observed only with solid, crystalline substances. Their behavior towards polarized light was such as to warrant the conclusion that these turbid liquids are anisotropic. In view of these facts, Lehmann proposed that liquids possessing these properties should be called *liquid crystals*, the term implying that, under ordinary conditions, the crystalline forces in these substances are so feeble that the crystals readily undergo deformation and actually flow like liquids. That these turbid liquids are not emulsions, is proven by the fact that when they are examined under the microscope, the turbidity is found to be due to the aggregation of a myriad of differently oriented transparent crystals. All subsequent investigation of liquid crystals has failed to show any lack of homogeneity. The number of such substances known at the present time is fairly large.

* Monatshefte, 9, 435 (1888).

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CHAPTER V

THE RELATION BETWEEN PHYSICAL PROPERTIES AND MOLECULAR CONSTITUTION

A large number of interesting and important relationships have been established between the physical properties of different chemical compounds and their molecular constitution.

While it is manifestly impossible to discuss more than a few of these relationships within the scope of this book, it is desirable that the student should at least be made familiar with the general character of investigations in this important branch of physical chemistry.

Before proceeding to a brief consideration of several typical examples illustrative of the dependence of physical properties upon molecular constitution, it should be pointed out that there are two different ways in which such relationships may be approached. Thus, we may seek to determine the influence which the number and kind of the atoms present in different molecules exert upon some particular physical property; or, on the other hand, we may strive to ascertain how the property in question is influenced by the manner in which the atoms are arranged in the molecule. The first method serves to bring out the *additive* character of the property, whilst the second method emphasizes its *constitutive* character. Almost all physical properties exhibit both additive and constitutive characteristics. In addition to additive and constitutive properties, Ostwald has introduced a third type which he calls *colligative* properties; the numerical value of colligative properties is entirely dependent upon the number of molecules present. For example, the volume of a gas is a colligative property since it is practically proportional to the total number of molecules present in the gas. Obviously, since colligative properties are independent of both composition and structure, they call for no further consideration in this chapter.

Molecular Volume. In dealing with the volume relations of liquids it is customary to employ the *molecular volume*, i.e., the volume occupied by the molecular weight of the liquid in grams. The justification for this procedure is, that when we compare the gram-molecular weights of liquids, the comparison involves equal numbers of molecules of the different substances.

Relations between the molecular volumes of liquids were first pointed out by Kopp.* On comparing the molecular volumes of different liquids at their boiling-points, he found that constant differences in composition correspond to approximately constant differences in the molecular volumes. Thus, the molecular volumes of the successive members of an homologous series differ by the same number of units, this difference corresponding, for example, to a CH_2 group. In like manner, the molecular volumes of various groups have been determined, and from these in turn the atomic volumes of the constituent elements have been worked out.

While Kopp found that his results were most regular when the molecular volumes were determined at the boiling temperatures of the respective liquids, the reason for this did not appear until after van der Waals had developed his theory of corresponding states. As has already been pointed out, the boiling-points of most liquids are approximately two-thirds of their respective critical temperatures, and therefore are corresponding temperatures.

Subsequent investigations have shown that the numerical values of the atomic volumes of the elements, as originally derived by Kopp, are more or less erroneous. The following values of the atomic volumes are those recently published by Le Bas† and represent the average values derived from the study of a large number of organic compounds of widely different character:

C = 14.8	Cl = 22.2	I = 37.0	N = 15.6	
H = 3.7	Br = 27.0	S = 25.6	= 10.5	(in primary amines)
O″ = 7.4	(as in aldehydes, ketones and doubly linked oxygen generally)		= 12.0	(in secondary amines)
O′ = 9.1	(in methyl esters)			
= 11.0	(in higher esters)	>O = 9.9	(in methyl ethers)	
= 12.0	(in acids)	= 11.0	(in higher ethers)	

As will be seen, the value of the atomic volume is dependent upon the manner of linkage of the atoms in the molecule.

By means of such a table of experimentally determined atomic volumes it is possible to calculate the molecular volumes of the

* Lieb. Ann., 41, 79 (1842); 96, 153, 303 (1855); 96, 171 (1855).

† The Molecular Volumes of Liquid Chemical Compounds.

lower members of the various homologous series of organic liquids with a fair degree of accuracy. For example, the molecular volume of acetic acid, $C_2H_4O_2$, may be calculated from the atomic volumes of its constituent atoms as follows: —

$$\begin{aligned} 2\ C &= 2 \times 14.8 = 29.6 \\ 4\ H &= 4 \times 3.7 = 14.8 \\ 1\ O' &= 1 \times 12.0 = 12.0 \\ 1\ O'' &= 1 \times 7.4 = 7.4 \end{aligned}$$

Molecular volume 63.8

The density of acetic acid at its boiling-point is 0.942 and its molecular weight is 60, therefore the observed value of the molecular volume is, 60/0.942 = 63.7, a result which is in excellent agreement with that calculated from the atomic volumes of the constituent atoms. The following table gives the calculated and observed values of the molecular volumes of a number of different organic compounds at their boiling-points: —

MOLECULAR VOLUMES
(Cubic centimeters per mol)

Substance.	Formula.	V_m (calc.)	V_m (obs.)
Methyl alcohol	CH_4O	38.7	42.0
Ethyl alcohol	C_2H_6O	60.9	62.0
Amyl alcohol	$C_5H_{12}O$	127.5	124.0
Acetaldehyde	C_2H_4O	51.8	56.5
Acetone	C_3H_6O	74.0	77.5
Formic acid	CH_2O_2	41.6	41.3
Acetic acid	$C_2H_4O_2$	63.8	63.7
Propionic acid	$C_3H_6O_2$	86.0	85.4
Methyl formate	$C_2H_4O_2$	63.8	63.4
Methyl acetate	$C_3H_6O_2$	86.0	85.8
Ethyl ether	$C_4H_{10}O$	106.1	106.0
Benzene	C_6H_6	111.0	96.0
Naphthalene	$C_{10}H_8$	177.6	149.2

It is apparent from the data of the foregoing table that while the agreement between the observed and calculated values of the molecular volumes is in some cases very satisfactory, in other cases the differences are so great as to engender doubt as to the purely additive character of this property. In fact, recent research has tended to restrict the application of Kopp's additive

generalization and to lay more emphasis upon the constitutive character of this property. In this connection, Le Bas writes: — "A study of molecular volumes has shown us that probably we are not at the end of the utility of physical properties as a means of giving us an insight into the structure of molecules. When a more scientific method of examination of these physical properties shall have been worked out, there is no doubt that a great advance will be made in our knowledge of the intricacies of chemical constitution."

Refractive Power of Liquids. The velocity of transmission of light through any medium depends upon its nature, especially upon its density. When a ray of light passes from one medium into another it is refracted, the degree of refraction being such that the ratio of the sines of the angles of incidence and refraction is constant and characteristic for the two media. This fundamental law of refraction was discovered by Snell about 1621. According to the wave theory of light, the ratio of the sines of the angles of incidence and refraction is identical with the ratio of the velocities of light in the two media. The ratio is termed the *index of refraction* and is usually denoted by the letter n. Representing by i and r, the angles of incidence and refraction, and by v_1 and v_2, the respective velocities of light in the two media, we have

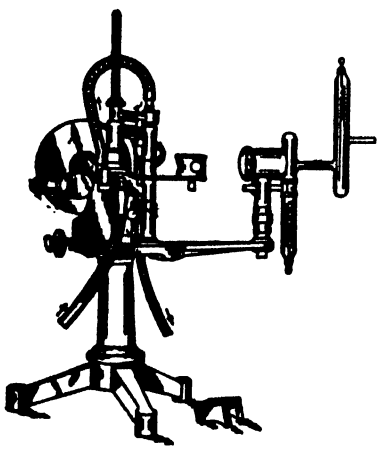


Fig. 41

$$n = \frac{\sin i}{\sin r} = \frac{v_1}{v_2}. \qquad (1)$$

Various forms of apparatus have been devised for the determination of the refractive index of liquids. Of these the best known and most satisfactory is the refractometer of Pulfrich, an improved form of which is shown in Fig. 41. While the limits of this book prohibit a detailed description of the apparatus, the fundamental principles involved in its construction will be readily understood

from the accompanying diagram, Fig. 42. The liquid or fused solid is placed in a small glass cell, C, which is cemented to a rectangular prism of dense optical glass, P, the refractive index of which is generally 1.61. A beam of monochromatic light, from a sodium flame, or a spectrum-tube containing hydrogen, is allowed to enter the prism in a direction parallel to the horizontal surface of separation between the glass and the liquid. After passing through the liquid and the prism, the beam emerges making an angle i with its original direction. By means of a telescope, the emergent beam can be observed and its position noted, the angle of emergence being read on a divided circle attached to the telescope. From the angle of emergence thus determined, the index of refraction of the liquid can be calculated in the following manner. The value of the index of refraction, N, for air/glass being known, we have

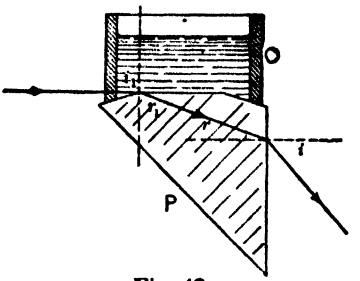


Fig. 42

$$N = \frac{\sin i}{\sin r}. \tag{2}$$

The angle of incidence of the last ray entering the prism from the liquid is 90°, or $\sin i_1 = 1$. The index of refraction, n_1, for liquid/glass may be calculated thus,

$$n_1 = \frac{\sin i_1}{\sin r_1} = \frac{1}{\sin r_1}. \tag{3}$$

But

$$\sin r_1 = \cos r = \sqrt{1 - \sin^2 r}. \tag{4}$$

Transposing equation (2) and substituting in equation (4), we have

$$\sin r_1 = \sqrt{1 - \frac{\sin^2 i}{N^2}},$$

or

$$\sin r_1 = \frac{1}{N}\sqrt{N^2 - \sin^2 i}. \tag{5}$$

Therefore, substituting equation (5) in equation (3), we have

$$n_1 = \frac{N}{\sqrt{\quad\quad}}. \tag{6}$$

Remembering that $n = N/n_1$, we have for the index of refraction, n, for air/liquid, by substitution in equation (6),

$$n = \sqrt{N^2 - \sin^2 i}, \tag{7}$$

or if $N = 1.61$,

$$n = \sqrt{2.5921 - \sin^2 i}. \tag{8}$$

The values of $\sqrt{N^2 - \sin^2 i}$ are generally given, for different values of i, in tables supplied with the refractometer, thus saving the experimenter a somewhat laborious calculation. The value of n thus obtained is the index of refraction from air into the liquid; if the index from vacuum into the liquid, the so-called *absolute index*, is required, the value of n must be multiplied by 1.00029.

The index of refraction is dependent upon temperature, pressure and in general upon all conditions which affect the density of the medium. Furthermore, it is dependent upon the wave-length of the light employed, the index for the red rays being less than that for the violet rays. It is therefore necessary in making measurements of refractive indices to use light of a definite wave-length, or what is termed *monochromatic light*. The sodium flame is most frequently used for this purpose, the wave-length being represented by the letter D. Measurements of the refractive index referred to the D-line of sodium are commonly designated by the symbol n_D. When incandescent hydrogen is employed as a source of light, the refractive index may be determined for the C-, F- and G-lines, the respective values being represented by n_C, n_F, and n_G.

Specific and Molecular Refraction. Various attempts have been made to express the refractive power of a liquid by a formula which is independent of variations of temperature and pressure. Of the different formulas proposed but two need be mentioned. The first, due to Gladstone and Dale,* is as follows: —

$$r_1 = \frac{n - 1}{d}, \tag{9}$$

in which d denotes the density of the liquid and r_1 is the so-called *specific refraction*. The other formula, proposed by Lorenz† and

* Phil. Trans. (1858).

† Wied. Ann., 11, 70 (1880).

Lorentz,* has the following form: —

$$r_2 = \frac{1}{d} \cdot \frac{n^2 - 1}{n^2 + 2}. \qquad (10)$$

This formula is superior to that of Gladstone and Dale which is purely empirical. It is based upon the electromagnetic theory of light and gives values of r_2 which are quite independent of the temperature. In order that we may compare the refractive powers of different liquids, the specific refractions are multiplied by their respective molecular weights, the resulting products being termed their *molecular refractions*. As the result of a large number of experiments, it has been shown that the molecular refraction of a compound is made up of the sum of the refractive constants of the constituent atoms, or in other words refractive power is an additive property. The values of the refractive constants of the elements and commonly-occurring groups have been determined with great care by Brühl and others, the method employed being similar to that used by Kopp in connection with his investigations on molecular volumes. Thus, Brühl found in the homologous series of aliphatic compounds that a difference of CH_2 in composition corresponds to a constant difference of 4.57 in molecular refraction. Then, having determined the molecular refraction of a ketone or an aldehyde of the composition, $C_nH_{2n}O$, he subtracted n times the value of CH_2 and obtained the atomic refraction of carbonyl oxygen. By deducting the molecular refraction of the hydrocarbon, C_nH_{2n+2}, from that of the corresponding alcohol, $C_nH_{2n+2}O$, he obtained the atomic refraction of hydroxyl oxygen. By subtracting six times the value of CH_2 from the molecular refraction of hexane, C_6H_{14}, he obtained the refractive constant for hydrogen or 2 H = 2.08. In like manner the refractions of other elements and groups of elements were determined.

Just as in the case of molecular volumes so with molecular refractions, the arrangement of the atoms in the molecule must be taken into consideration. Brühl,† who devoted much time to the investigation of the effect of constitution upon refraction, pointed out that the molecular refraction of compounds containing double and triple bonds is greater than the calculated value,

* Ibid., 9, 641 (1880).

† Proc. Roy. Inst., 18, 122 (1906).

and he assigned to these bonds definite constants of refraction. The values of the atomic refractions for a few of the elements are given in the following table.*

ATOMIC REFRACTIONS

Element	Gladstone and Dale Formula R_D	Lorenz and Lorentz Formula R'_D
Carbon singly bound and occurring alone, C·	4.71	2.592
Carbon singly bound, C'	4.71	2.501
Hydrogen, H	1.47	1.051
Hydroxyl oxygen, O'	2.65	1.521
Ethereal oxygen, O<	2.65	1.683
Ketonic oxygen, O''	3.33	2.287
Double bond, =	2.64	1.707
Triple bond, ≡	.....	2.10
Chlorine, Cl	10.05	5.998
Bromine, Br	15.34	8.927
Iodine, I	25.01	14.12

When applied to simple compounds of carbon, hydrogen and oxygen the agreement between the observed and calculated values of molecular refractions is generally very satisfactory. For example, we may compare the calculated and observed values of the molecular refraction of lactic acid, employing the Lorenz-Lorentz formula. The formula of lactic acid is, $CH_3CHOHCOOH$, or $C_3H_6O_2'O''$, hence the molecular refraction is calculated as follows: —

$$\begin{aligned} 3\,C &= 3 \times 2.501 = 7.503 \\ 6\,H &= 6 \times 1.051 = 6.306 \\ 2\,O' &= 2 \times 1.521 = 3.042 \\ 1\,O'' &= 1 \times 2.287 = 2.287 \\ \text{Molecular refraction} &= 19.138 \end{aligned}$$

The observed value of the molecular refraction of lactic acid is 19.138.

It has been found that the refractive power of a substance is influenced not only by the presence of double and triple bonds, but

* In this connection the student should consult a paper entitled "Atomic Refraction" by W. Swietoslawski in the Journal of the American Chemical Society, 42, 1945 (1920).

also by the relative position of such bonds within the molecule. When a molecule contains only one double or triple bond, the molecular refraction may still be calculated with considerable accuracy from the values of the atomic refractions, due allowance being made for the condition of unsaturation. When, however, a second double or triple bond is introduced into the molecule in a position adjacent to the first, the calculated value of the molecular refraction is found to differ appreciably from the observed value. This phenomenon is known as *optical anomaly.* In most cases the introduction of a second unsaturated group increases the molecular refraction and the substance is said to exhibit *optical exaltation;* in a few cases, however, the refractive power is diminished and the effect is then known as *optical depression.*

Where two unsaturated groups are separated by one or more saturated groups, optical anomaly is generally absent. Where unsaturated groups occupy such positions within the molecule that they exert mutual influence, they are said to be " conjugated." The anomalous behavior of organic compounds containing conjugated groups has been attributed by Thiele to the residual affinity or partial valence of the unsaturated carbon atoms. The following table gives the observed and calculated values of the molecular refraction of several organic compounds which exhibit optical exaltation.

MOLECULAR REFRACTIONS OF SOME UNSATURATED COMPOUNDS

Substance	Formula	MR'_D (calc.)	MR'_D (obs.)	Diff.
Mesityl oxide	$(CH_3)_2C = CH{\cdot}\overset{\displaystyle O}{\overset{\|}{C}}{\cdot}CH_3$	29.51	30.37	0.86
Benzalacetone	$C_6H_5{\cdot}CH = CH{\cdot}\overset{\displaystyle O}{\overset{\|}{C}}{\cdot}CH_3$	44.64	48.61	3.97
Benzalmethylethyl ketone	$C_6H_5{\cdot}CH = CH{\cdot}\overset{\displaystyle O}{\overset{\|}{C}}{\cdot}CH_2{\cdot}CH_3$	49.24	53.08	3.84
Benzalpinacolin	$C_6H_5{\cdot}CH = CH{\cdot}\overset{\displaystyle O}{\overset{\|}{C}}{\cdot}C(CH_3)_3$	58.44	62.77	4.33

The determination of the molecular refraction of a liquid affords a means of ascertaining or confirming its chemical constitution. For example, geraniol has the formula $C_{10}H_{18}O$, and its chemical behavior is such as to warrant the conclusion that it is a primary alcohol. The value of n_D is 1.4745, from which the molecular refraction is calculated to be 48.71. The molecular refraction calculated from the atomic refractions given in the preceding table is: —

$$\begin{aligned} 10\ \text{C} &= 10 \times 2.501 = 25.01 \\ 18\ \text{H} &= 18 \times 1.051 = 18.92 \\ 1\ \text{Hydroxyl O} &= 1 \times 1.521 = 1.52 \\ \text{Molecular refraction} & \qquad 45.45 \end{aligned}$$

The difference between the theoretical and experimental values of the molecular refraction is $48.71 - 45.45 = 3.26$, which is approximately twice the value of a double bond, $1.707 \times 2 = 3.414$. From this we conclude that the molecule of geraniol contains two double bonds. Furthermore an alcohol of the formula, $C_{10}H_{18}O$, containing two double bonds cannot possess a ring structure and therefore must be a member of the aliphatic group of compounds. This conclusion is supported by the chemical properties of the substance. The accepted structural formula of geraniol is

$$\begin{array}{l} \qquad\qquad\qquad\quad \text{H} - \text{C} - \text{CH}_2\text{OH} \\ (\text{CH}_3)_2\text{C} = \text{CH}\cdot\text{CH}_2\cdot\text{CH}_2 - \underset{\|}{\text{C}} - \text{CH}_3. \end{array}$$

In a similar manner the Kekulé formula for benzene has been confirmed, the difference between the theoretical and experimental values of the molecular refraction indicating the presence of three double bonds in the molecule.

Thus, Brühl* found that on changing from an acetylene to an ethylene linkage there is a decrease of 0.40 units in molecular refractive power, and also that in the polymerization of acetylene to benzene, as represented by the equation,

$$3\ \text{C}_2\text{H}_2 = \text{C}_6\text{H}_6,$$

a decrease of 1.19 units in refractive power occurs. Since the decrease in refractive power is approximately three times the change in refractive power resulting from the replacement of a

* Zeit. phys. Chem., 1, 343 (1887).

triple by a double bond, Brühl inferred that in a molecule of benzene there must be three double bonds as in the familiar formula proposed by Kekulé.

Specific Refraction of Mixtures. The specific refraction of an homogeneous mixture or solution is the mean of the specific refractions of its constituents. Thus, if the specific refractions of the mixture and its two components are represented by r_1, r_2, and r_3, then

$$r_1 = \frac{p}{100} r_2 + \frac{(100 - p)}{100} r_3, \tag{11}$$

where p denotes the percentage of the constituent whose specific refraction is r_2. Hence it is possible to determine the specific refraction of a substance in solution by measuring the refractive indices and densities of the solution and solvent. If the refractive indices of the solvent, solution and dissolved substance are represented by n_1, n_2, and n_3 respectively, and if d_1, d_2, and d_3 denote the corresponding densities, then we have

$$\frac{1}{d_3} \cdot \frac{n_3^2 - 1}{n_3^2 + 2} = \frac{100}{d_2 p} \cdot \frac{n_2^2 - 1}{n_2^2 + 2} - \frac{100 - p}{d_1 p} \cdot \frac{n_1^2 - 1}{n_1^2 + 2}, \tag{12}$$

where p is the percentage of the dissolved substance.

As has already been mentioned, the formula of Lorenz-Lorentz is based upon the electromagnetic theory of light. According to this theory $\frac{n^2 - 1}{n^2 + 2}$ expresses the fraction of the unit of volume of the substance which is actually occupied by it. From this it follows that the molecular refraction, $\frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$, is an expression of the volume actually occupied by the atomic nuclei of the molecule. It is interesting to note that the ratio of the sum of the atomic volumes, calculated by the method of Traube, to the corrected molecular volume, as determined by the Lorenz-Lorentz formula, is approximately constant, or

$$\frac{\Sigma \text{ atomic volumes}}{\frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}} = 3.45 \text{ approximately.} \tag{13}$$

This may be considered as the ratio of the volume within which the atoms execute their vibrations to their actual material volume.

Rotation of the Plane of Polarized Light. Some liquids when placed in the path of a beam of polarized light possess the prop-

erty of rotating the plane of polarization to the right or to the left. Such liquids are said to be *optically active*. Those substances which rotate the plane of polarization to the right are termed *dextro-rotatory*, while those which cause an opposite rotation are called *levo-rotatory*. The determination of the rotatory power of

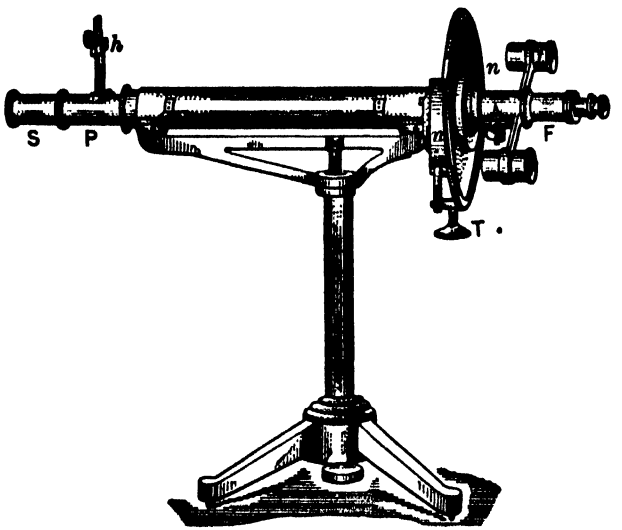


Fig. 43

a liquid is made by means of an instrument known as a *polarimeter*, a convenient form of which is shown in Fig. 43. The essential parts of this instrument are two similar Nicol prisms placed one behind the other with their axes in the same straight line as shown in Fig. 44. The light after passing through the forward prism,

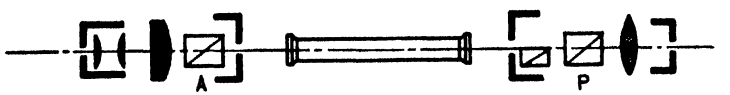


Fig. 44

P, known as the *polarizer*, has its vibrations reduced to a single plane; it is said to be plane polarized. On entering the rear Nicol prism, *A*, known as the *analyzer*, the light will either pass through or be completely stopped, depending upon the position of the prism. If the analyzer be slowly rotated, it will be observed that the positions of maximum transmission and extinction occur at points 90° apart. If the analyzer be rotated, so that its

axis is at right angles to the axis of the polarizer, the field observed will be dark, no light being transmitted. If now a tube similar to that shown in Fig. 45 be filled with an optically active liquid and placed between the polarizer and analyzer, the field will become light again, due to the rotation of the plane of polarization by the optically-active substance. The extent to which the plane of polarization has been rotated can be determined by turning the analyzer until the field becomes dark again, and reading on the divided circle, K, the number of degrees through which it has been moved. When it is necessary to turn the analyzer to the right, the substance is dextro-rotatory, and when it is necessary to turn it to the left, the substance is levo-rotatory. Various optical accessories have been added to the simple polarimeter described above to render the instrument more sensitive, but for these details the student must consult some special treatise.* The angle of rotation is dependent upon the nature of the liquid, the length of the column of substance through which the light passes, the wave-length of the light used, and the temperature at which the measurement is made. It is customary in polarimetric work to employ sodium light and, unless otherwise specified, it may be assumed that a given rotation corresponds to the D-line.

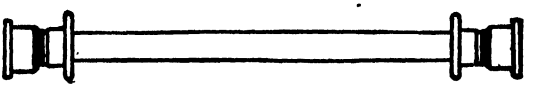


Fig. 45

Specific and Molecular Rotation. The results of polarimetric measurements are expressed either as specific rotations or as molecular rotations, the latter being preferable since the optical activities of different substances may then be compared.

The specific rotation is obtained by dividing the observed rotation by the product of the length of the column of liquid and its density,

or
$$[\alpha]_t = \frac{\alpha}{ld}, \tag{14}$$

where $[\alpha]_t$ is the specific rotation at the temperature t, α the observed angle, l the length of the column of liquid in decimeters, and d, its density. If the specific rotation is multiplied by the molecular weight of the substance, the molecular rotation is obtained, but owing to the fact that the resulting numbers are too large, it is customary to express the molecular rotation as one

* See for example, "The Optical Rotatory Power of Organic Substances and its Practical Applications." H. Landolt, trans. by J. H. Long.

one-hundredth of this value, thus

$$[\alpha_M]_t = \frac{M\alpha}{100\,ld}. \tag{15}$$

The specific and molecular rotations of solutions of optically active substances may also be determined, if we assume that the solvent is without effect. While this assumption is justifiable with aqueous solutions, it is not so when non-aqueous solvents are used. If g grams of an optically active substance be dissolved in v cc. of solvent, then

$$[\alpha]_t = \frac{\alpha v}{lg} \qquad \text{and} \qquad [\alpha_M]_t = \frac{M}{100} \cdot \frac{\alpha v}{lg}, \tag{16}$$

or, if the composition of the solution is expressed in terms of weight instead of volume, g grams of substance being dissolved in 100 grams of solution of density d, then

$$[\alpha]_t = \frac{100\,\alpha}{gdl}, \qquad \text{and} \qquad [\alpha_M]_t = \frac{M\alpha}{gdl}. \tag{17}$$

Optical Activity and Chemical Constitution. The fact that some substances have the power of rotating the plane of polarized light was first discovered by Biot, but the credit for recognizing the chemical significance of this fact belongs to Pasteur.* He discovered that ordinary racemic acid can be separated into two optically active modifications, one of which is dextro- and the other levo-rotatory, the numerical values of the two rotations being identical. If a solution of sodium ammonium racemate be allowed to evaporate at a low temperature, crystals of the composition $NaNH_4C_4H_4O_6.4\,H_2O$ will separate. On close inspection it will be found that the crystals are not all alike, but that they may be divided into two classes, one class showing some unsymmetrical crystal surfaces which are oppositely placed in the crystals of the other class. The crystals of one class may be regarded as the mirror images of those of the other class: such crystals are said to be *enantiomorphous*. The forms usually assumed by the two enantiomorphous modifications of sodium ammonium racemate are shown in Fig. 46. After separating the two forms Pasteur dissolved each in water, making the solutions of the same strength. The solution of the crystals with the

* Ann. Chim. Phys. (3), **24**, 442 (1848); **28**, 56 (1850); **31**, 67 (1851).

" right-handed faces " was found to be dextro-rotatory, while that of the crystals with the " left-handed faces " was found to be levo-rotatory. Pasteur then decomposed the two salts obtained from sodium ammonium racemate and obtained the corresponding acids, which he called dextro- and levo-racemic acids. It was subsequently shown that the two acids were identical with dextro- and levo-tartaric acids. Finally, when Pasteur mixed equivalent amounts of concentrated solutions of dextro- and levo-tartaric acids, an appreciable evolution of heat was observed, indicating that a chemical reaction had taken place. After allowing the solution to stand for some time, crystals of ordinary racemic acid were obtained.

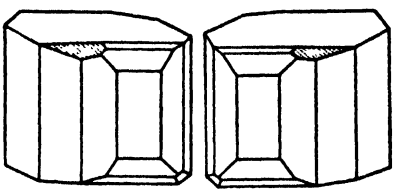


Fig. 46

Thus it was clearly proven that an optically inactive substance may be separated into two optically active modifications, possessing equal and opposite rotatory powers, and that by mixing equivalent quantities of the two optically active forms, the optically inactive substance may be recovered.

Pasteur discovered and applied three other methods, in addition to the mechanical method already described, for the separation of a substance into its optically active modifications. These are as follows: — (a) *Method of Crystallization;* (b) *Method of Formation of Derivatives;* and (c) *Methods of Ferments.*

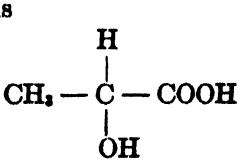
Methods of Crystallization. To a supersaturated solution of the racemic modification, a very small crystal of one of the active forms is added. This will induce the separation of crystals of the same form, inoculation with a dextro-crystal producing the dextro-form and inoculation with a levo-crystal producing the levo-form.

Method of Formation of Derivatives. In this method an optically active substance, generally an alkaloid, is added to the racemic modification, producing optically active derivatives having different solubilities. Thus if cinchonine, an optically active alkaloid having the formula, $C_{19}H_{22}N_2O$, be added to the racemic modification of tartaric acid, the cinchonine salt of the levo-acid will crystallize first. The crystals of the cinchonine salt are then removed and, after adding ammonia to displace the alkaloid,

dilute sulphuric acid is added and the pure levo-tartaric acid is obtained.

Methods of Ferments. Notwithstanding the fact that optical antipodes resemble each other so closely in most of their properties, Pasteur found that certain micro-organisms have the power of distinguishing sharply between these forms. For example, if *penicillium glaucum* be introduced into a solution of racemic tartaric acid, it thrives at the expense of the dextro-acid and eventually leaves the pure levo-form. In this method, one of the active modifications is always lost.

Pasteur was the first to point out that there must be some intimate connection between optical activity and the constitution of the molecule. It remained for Le Bel* and van't Hoff,† however, to formulate independently and almost simultaneously an hypothesis to account for optical activity on the basis of molecular constitution. Their important work laid the foundation of spatial chemistry, commonly termed *stereochemistry*. Le Bel accepted Pasteur's view that optical activity is dependent upon a condition of asymmetry, but whether this asymmetry is a property of the crystal alone, or whether it belongs to the molecule of the optically active substance, was the question he set himself to answer. He found, on dissolving certain optically active crystals in an inactive solvent, that the optical activity is imparted to the solution and therefore he concluded that the condition of asymmetry must exist in the chemical molecule. All of the optically active substances known to Le Bel were compounds of carbon. An examination of the formulas of these compounds led him to ascribe the cause of their optical activity to the presence of an *asymmetric* carbon atom, that is, a carbon atom combined with four different atoms or groups of atoms. One of the simplest examples is afforded by lactic acid, the structural formula of which is



In this formula the asymmetric carbon atom is placed at the center and is in combination with hydrogen, hydroxyl, methyl

* Bull. Soc. Chim. (2) **22**, 337 (1874).

† Ibid. (2), **23**, 295 (1875).

and carboxyl. In connection with his work on the relation between optical activity and asymmetry, Le Bel pointed out that active forms never result from laboratory syntheses, the racemic modification being invariably obtained. Van't Hoff reached conclusions similar to those of Le Bel and proposed the additional theory of the *asymmetric tetrahedral carbon atom.* Since the four valences of the carbon atom are equivalent, as the work of Henry on methane has shown them to be, van't Hoff pointed out that the only possible geometrical arrangement of the atoms in the molecule of methane must be that in which the carbon atom is placed at the center of a regular tetrahedron with the four hydrogen atoms at the four apices. He also pointed out that when the four valences of the tetrahedral carbon atom are satisfied with different atoms or groups, no plane of symmetry can be passed through the figure, the carbon atom being asymmetric. This conception of Le Bel and van't Hoff forms the basis of

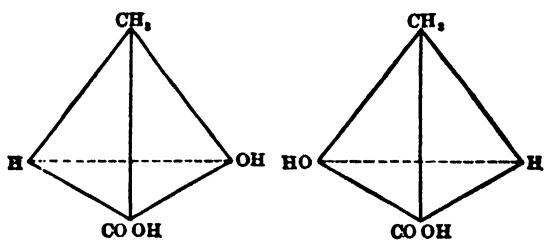
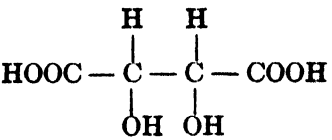


Fig. 47

stereochemistry, and has proved of inestimable value to the organic chemist in enabling him to explain the existence of many isomeric compounds. Thus, ordinary lactic acid can be split into two optically active isomers. Aside from the fact that one acid is dextro- and the other is levo-rotatory, the properties of the two acids are practically identical. If the formulas are written spatially, the different groups can be arranged about the asymmetric carbon atom in such a way that the two tetrahedra shall be mirror images of each other, as shown in Fig. 47. It will be observed that these two tetrahedra can in no way be superposed so that the same groups fall over each other, that is to say, they are enantiomorphous forms. In tartaric acid there are two asymmetric carbon atoms as is evident when its structural formula is written as follows:—



If the stereochemical formulas of the dextro- and levo-acids be represented as in Fig. 48, (a) and (b), it will be apparent that the theory admits of the existence of another isomer with the atoms and groups arranged as in Fig. 48 (c).

In this arrangement the asymmetry of the upper tetrahedron is the reverse of that of the lower, and consequently the optical activity of one-half of the molecule exactly compensates the optical activity of the other half, and the molecule as a whole is inactive. It is evident that such a tartaric acid could not be split into two active forms. Actually there are four tartaric acids known, viz.,

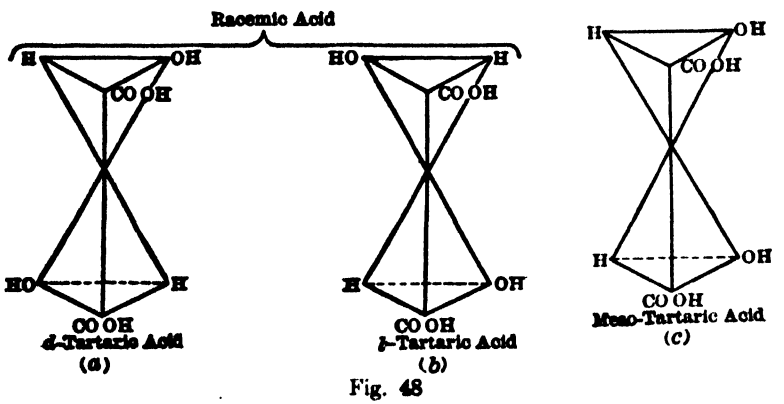
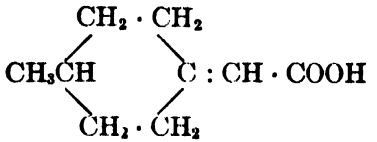


Fig. 48

(1) inactive racemic acid which is separable into (2) dextro-tartaric acid and (3) levo-tartaric acid; and (4) meso-tartaric acid, an inactive substance which has never been separated into two active forms, but which has the same formula, the same molecular weight and in general the same properties as the dextro- or levo-tartaric acids. Inactive forms, such as meso-tartaric acid, are said to be inactive by *internal compensation*. This constitutes one of many beautiful confirmations of the van't Hoff theory of the asymmetric tetrahedral carbon atom.

Meso-tartaric acid furnishes an illustration of the fact that asymmetric carbon atoms may be present in the molecule without imparting optical activity to the substance. The converse

of this proposition, however, that optical activity is dependent upon asymmetric carbon atoms, is generally true. Certain substances which apparently contain no asymmetric carbon atoms have been discovered which are, nevertheless, optically active. An example of such a substance is 1-methyl cyclohexylidene-4 acetic acid, to which the following formula has been assigned: —



Other atoms aside from carbon may be asymmetric; thus certain compounds of nitrogen, sulphur and tin have been shown to be optically active. The theory also furnishes an explanation of the fact, pointed out by Le Bel, that optically active forms are never obtained by direct synthesis. Since the rotatory power is dependent upon the arrangement of the atoms and groups in the molecule, it follows from the doctrine of probability that as many dextro as levo configurations will be formed, and consequently the racemic modification will be obtained.

Up to the present time no satisfactory generalization has been discovered as to the factors determining the molecular rotation in any particular case. An attempt in this direction has been made by Guye,* in which he ascribes the magnitude of the observed rotation to the relative masses of the atoms or groups which are in combination with the tetrahedral carbon atom. But it cannot be mass alone which conditions optical activity, since substances are known which rotate the plane of polarization, notwithstanding the fact that their molecules have two groups of equal mass in combination with the asymmetric carbon atom. The molecular rotations of the members of homologous series exhibit some regularities, but on the other hand many exceptions occur which cannot be satisfactorily explained. About all that can be said at the present time is, that optical activity is a constitutive property.

Magnetic Rotation. That many substances acquire the power of rotating the plane of polarized light when placed in an intense magnetic field was first observed by Faraday† in 1846.

* Compt. rend., 110, 714 (1890).

† Phil. Trans., 136, 1 (1846).

The relation between chemical composition and magnetic rotatory power has since been investigated very exhaustively by W. H. Perkin,* his experiments in this field having been continued for more than fifteen years. In brief, Perkin's method of investigating magnetic rotatory power consisted in introducing the liquid to be examined into a polarimeter tube 1 decimeter in length and then placing the tube axially between the perforated poles of a powerful electromagnet, as shown in Fig. 49. Upon exciting the magnet it was found that the plane of polarization was rotated, either to the right or the left, the direction of rotation depending upon the direction of the current, the intensity of the magnetic field and the nature of the liquid. Perkin used the sodium flame as his source of light and carried out all of his experiments at 15° C. He expressed his results by means of the formula, $M\alpha/d$, α being the observed angle of rotation, d the density of the liquid and M its molecular weight. All measurements were expressed in terms of water as a standard: thus if $M\alpha/d$ is the rotation for any substance, and $M'\alpha'/d'$ is the corresponding rotation for water, then, according to Perkin, the *molecular magnetic rotation* will be given by the ratio, $M\alpha/d : M'\alpha'/d'$, or $M\alpha d'/M'\alpha' d$.

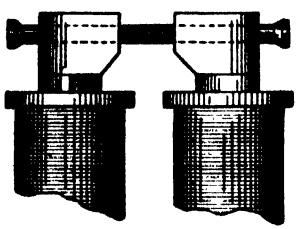


Fig. 49

The molecular magnetic rotation for a large number of organic compounds has been determined by Perkin, who has shown it to be an additive property. In any one homologous series the value of the molecular magnetic rotation is given by the formula,

$$\text{mol. mag. rotation} = a + nb, \qquad (18)$$

where a is a constant characteristic of the series, b is a constant corresponding to a difference of CH_2 in composition, its value being 1.023, and n is the number of carbon atoms contained in the molecule. This formula is applicable only to compounds which are strictly homologous, isomeric substances in two different series giving quite different rotations. The constitution of the molecule exerts as great an influence on magnetic rotation

* Jour. prakt. Chem. [2], 31, 481 (1885); Jour. Chem. Soc., 49, 777; 41, 806; 53, 561, 695; 59, 981; 61, 287, 800; 63, 57; 65, 402, 815; 67, 255; 69, 1025 (1886–1896).

as it does on refraction, a double bond causing an appreciable increase in the value of a. The results of experiments on magnetic rotation show that nothing like the same regularities exist as have been discovered for molecular refraction and molecular volume. The rotatory powers of various inorganic substances have been determined, but the results are too irregular to admit of any satisfactory interpretation.

Absorption of Light. When a ray of light traverses any transparent or translucent medium, a portion of the radiant energy is absorbed and the emergent ray is poorer by the vibrations which have been taken up. The spectrum of the emergent light is characterized by dark bands corresponding to the wave lengths of the incident light which have been absorbed. Such a spectrum is known as an *absorption spectrum*, and is characteristic for each individual substance under specified conditions. The phenomenon of absorption is exhibited by gases, liquids and solids. In the case of solids, however, the opacity is so great that incident radiation can only penetrate a short distance below the surface. The characteristic absorption of a solid may be determined, nevertheless, by observing the spectrum of the light reflected from its surface. With liquids and gases there is no difficulty in determining the absorption by direct transmission.

Two distinct types of absorption are recognized, namely, *general* and *selective* absorption. In the former, the intensity of the transmitted light is diminished equally throughout the entire region of the spectrum under observation, whereas in the latter there are marked inequalities in the intensity of the transmitted light, resulting in the formation of bands of varying width in different parts of the spectrum. It often happens that both general and selective absorption occur together in the same spectral region and, when this is the case, the selective absorption is apt to be masked by the general absorption. Owing to the greater persistence of selective absorption, however, the effect of general absorption may be practically eliminated by diluting the substance with a non-absorbing solvent and thus lessening the number of absorbing units in the path of the incident light.

The pioneer investigator in this field of research was W. N. Hartley, and to him we owe the first succinct statements as to the probable mechanism of the absorption of radiant energy by individual chemical substances. He suggested that the cause of

absorption is to be traced to the movements of particles within the absorbing medium. As the result of his studies on the effect of temperature and pressure on the absorption spectra of various vapors, Hartley* concluded that general absorption is due to the damping effect of the molecules of the medium on the incident light waves. According to this view, the hope of finding any definite connection between general absorption and chemical constitution is rather remote. From his observations on selective absorption, Hartley concluded that this type of absorption is a resonance phenomenon in which the submolecular particles of the absorbing medium vibrate synchronously with the incident light waves.† Thus, if a beam of sunlight traverses an absorbing medium and the wave lengths of the absorbed radiation be measured, it should be possible to estimate the approximate frequencies of the vibration of the sub-molecular particles which constitute the medium. In his discussion of the phenomenon of absorption and the nature of the sub-molecular particles to which it is due, Hartley advanced the idea that the vibrating particles, or resonators, are either atoms or atomic complexes. This view was commonly accepted until early in the present century when Drude,‡ as the result of a mathematical treatment of the phenomena of dispersion and absorption from the standpoint of the electron theory, showed that the vibrations corresponding to the ultra-violet and most of the visible spectrum are due to electrons whose mass bears to their charge a constant ratio. He further pointed out that the number of these electrons in saturated compounds corresponds very closely to the total number of valences of their constituent elements. It follows, therefore, that the vibrating particles, or resonators, which cause absorption in the ultra-violet and visible regions of the spectrum are valence electrons. Drude subsequently showed that selective absorption in the infra-red region is caused by positively charged particles whose mass is comparable with that of atoms.

The energy of the radiation absorbed by a medium may be expended in one of the three following ways: — (1) In raising the temperature of the medium, (2) in causing the medium to

* Hartley, Jour. Chem. Soc., 39, 153 (1881); 95, 52 (1909).

† Hartley's explanation of the phenomenon of absorption is not in accord with the modern view involving the displacement of electrons.

‡ Drude, Drude's Ann., 14, 677, 936 (1904).

become fluorescent, or (3) in initiating chemical changes in the medium.

Measurement of Absorption. Numerous methods for the measurement of absorbed radiation have been developed but, in general, it may be said that the selection of a method applicable to any particular problem is dependent upon the region of the spectrum to be examined. While all of the methods for the measurement of absorption are based upon the same underlying principles, they differ from one another in the manner in which the absorption is detected. Thus, absorption in the visible region of the spectrum may be readily detected by the eye, while the photographic plate must be employed in the ultra-violet region. In the infra-red, absorption is detected by means of a sensitive thermopile or radiometer, since neither the eye nor the photographic plate is sensitive to infra-red radiation. The three units and symbols commonly used in measurements of wave length together with their relative magnitudes are given in the following table.

UNITS OF WAVE LENGTH

Unit.	Symbol.	Millimeters.	Relative length.
Ångström	Å	one ten millionth	1
Millimicron	$m\mu$	one millionth	10
Micron	μ	one thousandth	10,000

It should be pointed out that, in all measurements of absorption, the absorbing substance should be dissolved in a solvent which does not exhibit absorption in the region to be examined. Furthermore, it must be borne in mind that although the solvent may be non-absorbing, it frequently exerts a marked physical influence on the spectrum of the dissolved substance. For it has been shown by Kundt* that, as the refractive index of a solvent increases, the absorption bands of a dissolved substance undergo a shift toward the less refrangible end of the spectrum. For this reason it is important to employ the same solvent throughout any series of experiments where comparisons of the results are to be made.

* Kundt, Wied. Ann., 4, 34 (1878).

In order that the results of the spectroscopic examination of different substances may be comparable, it is necessary to employ solutions of known molecular concentration. It is customary to follow Hartley's recommendation that the molecular weight of the substance in milligrams be dissolved in a definite volume of solvent. Assuming the validity of Beer's law (see p. 634), the change in absorption with dilution may be followed by examining the spectrum of decreasing thicknesses of the original solution.

According to Beer's law the absorption of light is such that the product of the thickness t, of an absorbing layer of solution of molar concentration m, is constant, or $mt = k$. If, then, the thickness of a given layer of solution is diminished n times, its absorption will be the same as that of a solution whose concentration is only $1/n$th of that of the original solution. Thus, by varying the thickness of the absorbing layer we produce the same

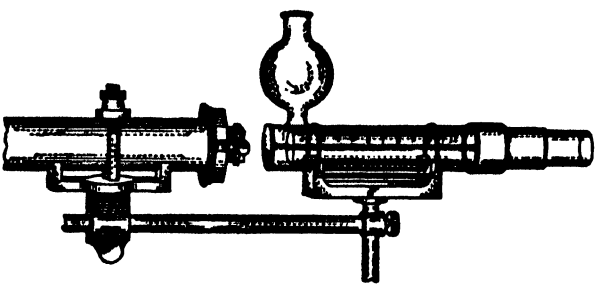


Fig. 50

effect as by changing the concentration, and by progressively reducing the length of the absorbing column we ultimately reach a point where the solution ceases to absorb.

The convenient device of Baly for altering the length of the absorbing column of liquid is shown in Fig. 50, attached to the collimator of the spectrograph. It consists of two closely-fitting tubes, one end of each tube being closed by a plane, quartz disc. The outer tube is fitted with a small bulbed-funnel and is graduated in millimeters. The two tubes are joined by means of a piece of rubber tubing which prevents leakage of the contents, and at the same time admits of the adjustment of the column of liquid to the desired length by simply sliding the smaller tube in or out. In this manner it is possible to record on a single photo-

graphic plate an entire series of spectra showing the change in absorption resulting from a progressive diminution in the number of absorbing molecules in the path of the incident radiation.

A convenient method of graphic representation of spectroscopic data was devised by Hartley. He proposed that the wave lengths, or their reciprocals, the wave numbers, corresponding to the limits of the absorption bands be plotted against the thicknesses of the solution in millimeters. The curve thus obtained he called the "curve of molecular vibrations" of the dissolved substance. Owing to the fact that the curves plotted in the above manner are frequently very extended, Baly and Desch* proposed that in-

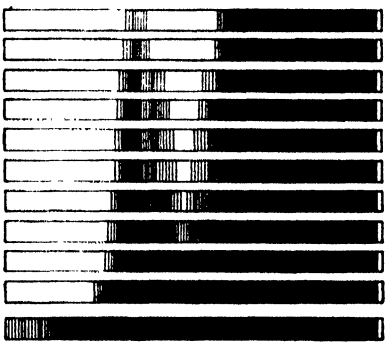


Fig. 51

stead of plotting thicknesses of solution as ordinates, logarithms of the thicknesses should be substituted. The latter method of plotting is the one which is now almost universally adopted.

The following example will serve to illustrate the method of plotting a curve of molecular vibration from a series of absorption spectra. In Fig. 51 is shown a series of absorption spectra of ten different thicknesses of a solution of sulphanilic acid in water. The uppermost spectrum corresponds to a 50 mm. column of 0.001 *m* $C_6H_4.NH_2.SO_3H$ while the succeeding strips represent the absorption spectra resulting from diminishing the thickness of the absorbing layer by uniform steps of 5 mm. The lowest spectrum is that of the source of light alone. Applying a scale of wave lengths, or making use of a curve of calibration of the

* Baly and Desch, Jour. Chem. Soc., 85, 1039 (1904).

prism of the spectrograph, the positions of the limits of absorption are determined and laid off as abscissas against the logarithms of the corresponding thicknesses in millimeters. In this manner the curve of molecular vibration shown in Fig. 52 is obtained. It will be seen from the diagram that maximum absorption occurs at a frequency, or wave number, $n = 358$. This minimum in the curve which represents maximum absorption is commonly known as the "head of the band." The resistance of the absorption band to dilution, termed the "persistence of the band," is measured by the depth of the band; in the diagram this will be observed to extend from 1.0 to 1.7 units of the logarithmic scale.

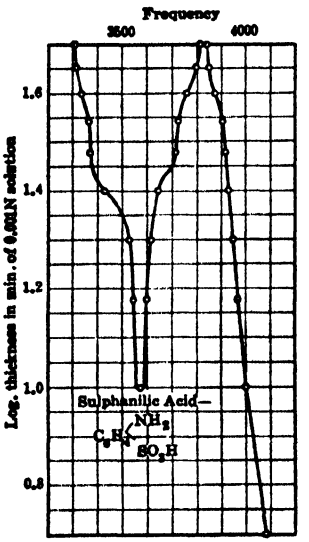


Fig. 52

The quartz spectrograph with which the absorption spectra shown in Fig. 51 were obtained, is represented diagrammatically in Fig. 53. Light from a suitable source, A, is concentrated upon the slit, S, of the spectrograph by means of a quartz condensing lens L. The solution to be examined is placed in the Baly tube, C, and then interposed between A and S. After traversing the solution, the rays of light enter the slit of the collimator of the spectrograph where, by means of a quartz lens, they are rendered parallel before striking the quartz prism P. The latter consists of two 30° half-prisms placed face to face, one prism being cut from a right-handed, and the other from a left-handed, crystal of quartz in such a manner as to bring the optic axis parallel to the base of each half-prism. This type of prism was devised by Cornu in order to eliminate the doubling effect due to the polarizing action of quartz on the emergent beam. The refracted and dispersed rays then enter the camera, B, where the spectrum is photographed on the plate D. The plate holder is fitted with a rack and pinion by means of which the plate may be moved through measured distances in a vertical plane, thus enabling the experimenter to photograph a number of spectra on the same plate. The instrument may also be provided with a specially calibrated,

transparent wave-length scale which can be brought in direct contact with the plate and photographed above or below the spectra as desired. This device enables one to read the wave-lengths corresponding to the limits of absorption directly from the

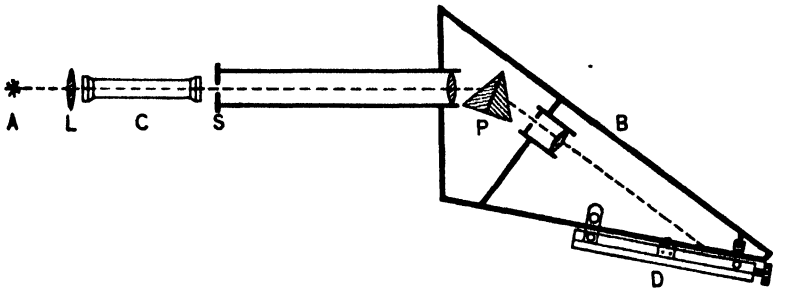


Fig. 53

plate, thus avoiding the necessity of preparing a special calibration curve for the instrument.

The source of light to be employed varies with the character of the investigation; in some cases an iron arc proves satisfactory and in other cases a condensed spark between suitable electrodes

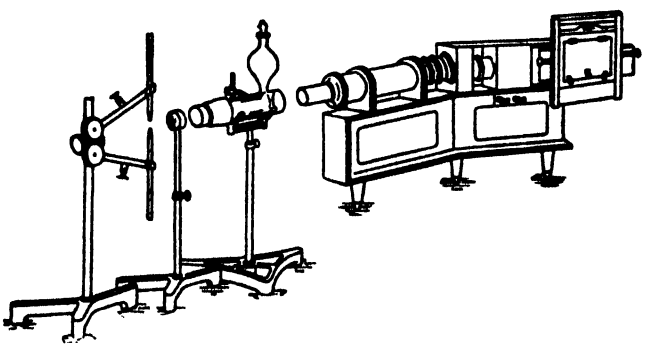


Fig. 54

is preferable. The assembled apparatus is shown in Fig. 54.

Spectrophotometry. In 1908, Kayser* called attention to the fact that the results obtained by the method just outlined are at best only semi-quantitative, since not only the intensities but also

* Kayser, Handbuch der Spektroskopie, Band 3, p. 49.

the positions of the maxima of the absorption bands remain undetermined until quantitative measurements of the extinction coefficient for each wave length have been made. By the extinction coefficient is meant the quantity,

$$e = \frac{1}{d} \log \frac{I}{I_0}, \tag{19}$$

where I_0 is the intensity of the incident light and I the intensity of the light after it has traversed a thickness, d, of the absorbing medium. Instruments designed for the measurement of extinction coefficients are known as spectrophotometers. In the succeeding paragraphs we shall briefly describe spectrophotometers adapted to measurements in the visible, ultra-violet and infra-red regions of the spectrum.

Spectrophotometry in the Visible. One of the most satisfactory instruments for spectrophotometric measurements in the visible

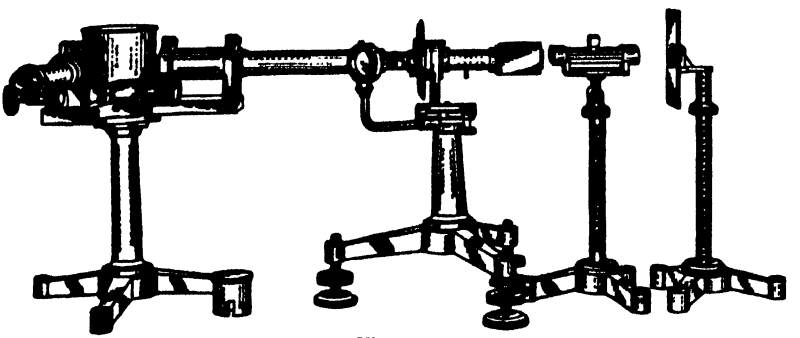


Fig. 55

region of the spectrum is that designed by Nutting.* The Nutting spectrophotometer as used in conjunction with a constant deviation wave-length spectrometer, is shown in Fig. 55, while a diagrammatic representation of the optical system is shown in Fig. 56. The light from a small incandescent lamp L, enclosed in a suitable housing, is split into two parallel beams by means of the two prisms P, P'. One of the beams then passes through the cell, C, containing the absorbing solution, while the other traverses an exactly similar cell containing the solvent. Both beams then

* Nutting, Bull. Bureau of Stand., 7, 239 (1910).

enter the photometer, the lower beam traversing the Nicol prism, N_1, where it becomes polarized, while the upper beam is brought into close juxtaposition with the lower beam by means of reflecting prisms. Both upper and lower beams then traverse a second Nicol prism, N_2, before they emerge from the photometer. The construction of the instrument is such that there is projected upon the slit, S, of the constant deviation wave-length spectrometer,

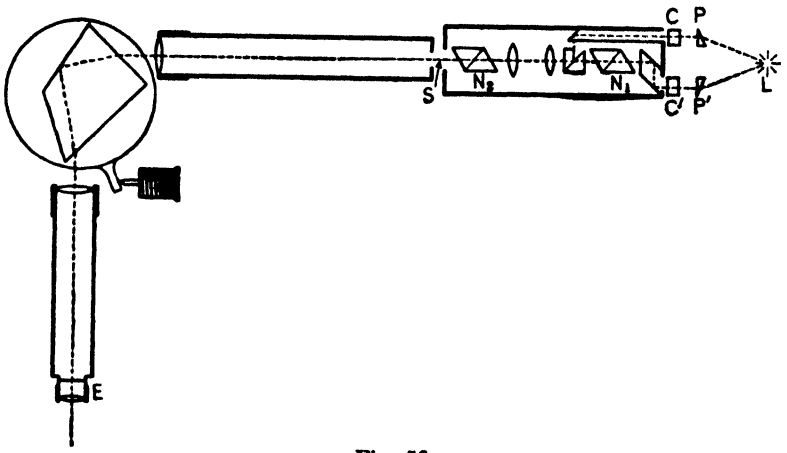
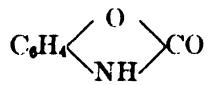


Fig. 56

a tri-partite field, of which the two outer portions are illuminated by the light which has undergone absorption by the solution in C and traversed the Nicol prism, N_2, while the intermediate portion of the field is illuminated by the light which has passed through the solvent and both Nicol prisms, N_1 and N_2. Since the light which has traversed the solution and the Nicol prism, N_1, is polarized, its intensity can be altered by rotating the prism, N_2. On observing the resulting spectrum in the eye-piece, E, of the spectrometer, one sees a spectrum divided into three horizontal strips in close juxtaposition, of which the two outer strips are reduced in intensity in consequence of the absorption of the solution. The intensity of the intermediate strip can readily be reduced to match that of the two outer strips, for any portion of the spectrum, by rotating the Nicol prism, N_2. Attached to the latter is a divided circle (not shown in the diagram) which is graduated to give the values of log I/I_0 directly. When a perfect match is obtained for a particular wave-length, the value of the extinction coeffi-

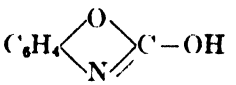
cient is easily determined by dividing the reading on the graduated circle by the thickness of the absorbing layer in centimeters.

Absorption and Constitution. The systematic investigation of the ultra-violet absorption spectra of organic compounds has proven of great value in establishing the structure of numerous compounds of uncertain chemical constitution. The importance of this type of research has been abundantly demonstrated by the results of the investigations of Hartley, Baly, Desch, Dobbie, Stewart and others. A few illustrations of the relation of curves of molecular vibration to chemical constitution must here suffice. We will take the case of o-hydroxy-carbanil; the constitution of this substance was known to be represented by one of the two following formulas: — *



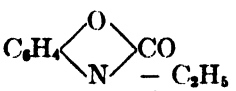
(*a*)

or

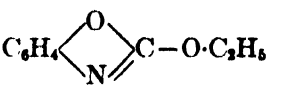


(*b*)

On comparing the curves of molecular vibration for the three substances (Fig. 57), it is apparent that the curves for the lactam ether and o-hydroxy-carbanil bear a close resemblance to each other, while the curve for the lactim ether is very different from the curves for the other two substances. The constitution of o-hydroxy-carbanil must then be very similar to that of the lactam ether. The formulas of the ethyl derivatives of the mother substance are known to be as follows: —



Lactam ether



Lactim ether

Hartley concluded, therefore, that formula (*a*) represents the structure of the molecule of o-hydroxy-carbanil.

Another interesting example of the application of ultra-violet absorption spectra to the determination of chemical constitution is afforded by compounds containing the keto-methylene group, $-CH_2-CO-$. Baly and Desch,† as the result of an extensive examination of the absorption spectra of compounds con-

* Hartley, Dobbie and Paliatseas, Jour. Chem. Soc., **77**, 839 (1900).

† Baly and Desch, Jour. Chem. Soc., **85**, 1029 (1904); **87**, 766 (1905).

taining the keto-methylene group, found that, although all of the metallic salts of these compounds exhibited well-defined selective absorption, the majority of the parent substances showed only general absorption. The absorption curves of acetyl acetone, $CH_3COCH_2COCH_3$, and its metallic derivatives are all quite

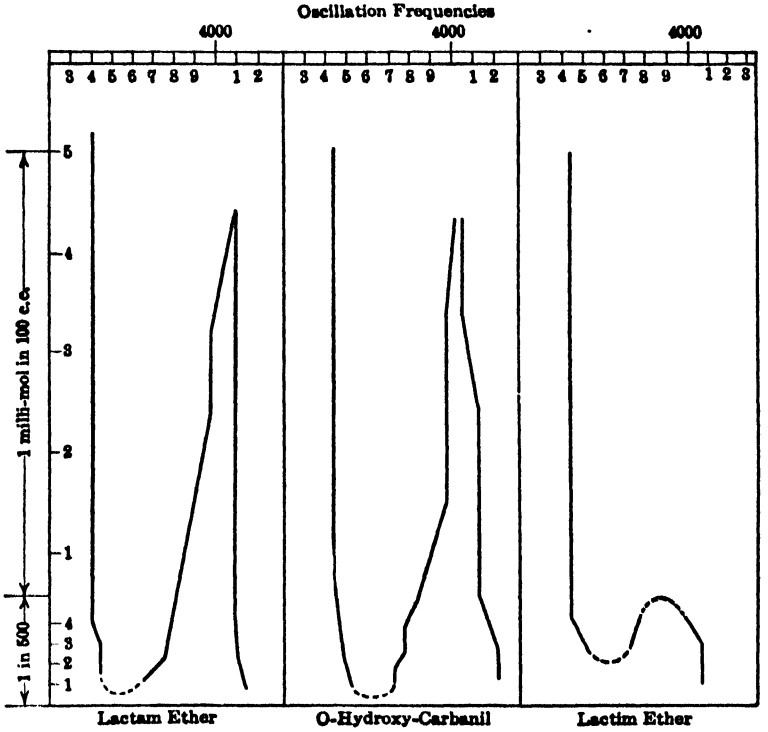


Fig. 57

similar, as will be seen from Fig. 58. It is probable, therefore, that the metallic salts and the parent substance are structurally identical and, since the salts are commonly regarded as possessing the enolic form, it might be inferred that selective absorption is characteristic of enolic compounds in general. Hartley, however, had failed in his examination of a large number of aliphatic alcohols and ethylenic compounds to discover a single example of selective absorption.

In order to settle the question, Baly and Desch* undertook the

* Baly and Desch, Jour. Chem. Soc., 85, 1029 (1904); 87, 766 (1905).

study of the oxygen-ethyl derivatives of various enolic compounds, such as,

$$CH_3\cdot C(OC_2H_5) = CH\cdot COOC_2H_5 \quad \text{and} \quad H_5C_2OOC = CHCOOC_2H_5.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OC_2H_5$$

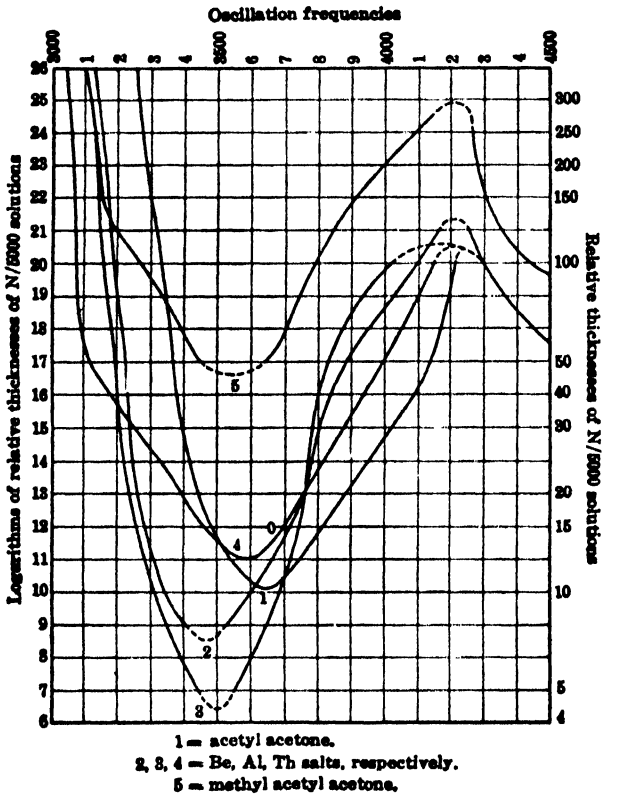
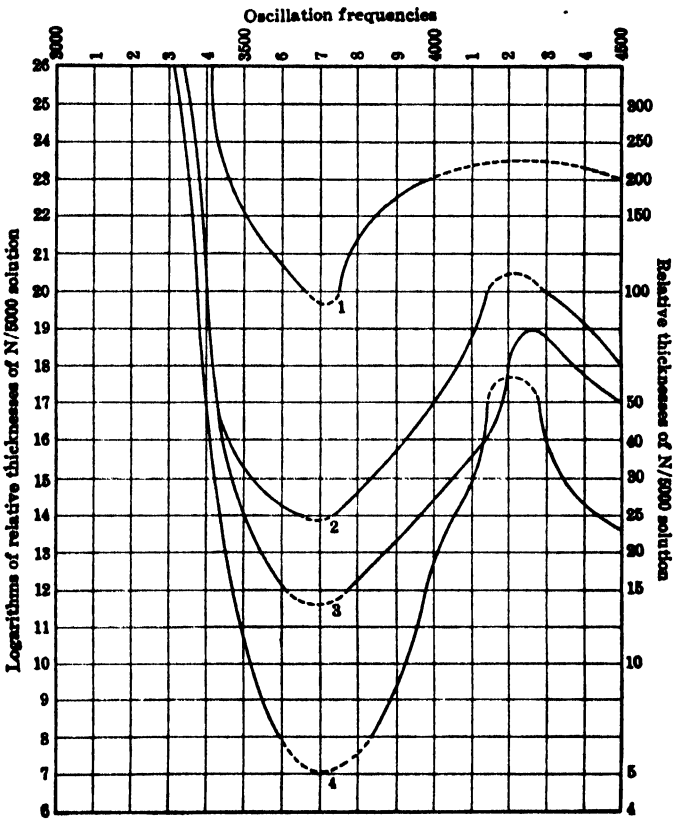


Fig. 58

These substances were found to exhibit only general absorption, from which fact Baly and Desch concluded that the cause of selective absorption cannot be ascribed to enolic structure. Furthermore, since mixtures of enolic and ketonic isomerides are known to exhibit general absorption only, the possibility of combination between the two forms is excluded. Consequently, the only remaining possibility is that the selective absorption of these

compounds is connected with the tautomeric change from one form to the other.

That this conclusion is correct is proven by the alteration in the absorption curves of acetoacetic ester, $CH_3CO{\cdot}CH_2COOC_2H_5$, produced by the addition of increasing amounts of sodium hydroxide.



1. Acetoacetic ester + 1 equiv. alkali.
2. Acetoacetic ester + ½ equiv. alkali.
3. Aluminium compound of acetoacetic ester.
4. Acetoacetic ester and excess of alkali.

Fig. 59

It is a well established fact that the addition of sodium hydroxide, or other alkaline hydroxide, to acetoacetic ester promotes this tautomeric transformation. Since this is equivalent to saying

that the addition of alkali increases the number of molecules undergoing change, it follows that there should be a corresponding increase in the intensity and persistency of the absorption.

That this is actually the case is shown by the curves in Fig. 59, in which (1) and (2) represent the absorption curves of acetoacetic ester with one-half and one equivalent of alkali respectively, while (4) is the curve obtained with an excess of alkali. Curve (3) represents the absorption of the corresponding aluminum compound. These results confirm the view that the absorption band which is developed in acetoacetic ester, and related substances, by the addition of alkali is to be attributed to an oscillation between the two tautomeric forms, which may be represented as follows: —

$$-CH_2.CO- \rightleftarrows -CH = C(OH)-.$$

From the foregoing paragraphs it is evident, therefore, that samples of the ester which fail to exhibit selective absorption must be pure specimens of one or the other of the two tautomeric forms.

The systematic examination of the absorption spectra of the alkaloids has resulted in the solution of a number of problems in connection with the chemical constitution of this group of exceedingly complex compounds. Thus, it has been found that the absorption bands of quinine, cocaine and morphine are practically identical with those of 6-methoxyquinoline-benzoic acid and catechol, while the absorption spectra of emetine, corydaline and laudanosine also reveal the presence of the catechol grouping.

Dielectric Constants and Absorption of Electric Vibrations. Faraday discovered that the attraction or repulsion between two electric charges varies with the nature of the intervening medium, or dielectric. If q_1 and q_2 represent two charges which are separated by a distance, r, the force of attraction or repulsion, f, is given by the equation,

$$f = \frac{1}{D} \cdot \frac{q_1 q_2}{r^2}, \tag{20}$$

where D is a specific property of the medium known as the *dielectric constant*. The dielectric constant of air is taken as unity. Various methods have been devised for the experimental determina-

tion of the dielectric constant, but the scope of this book forbids a description of the apparatus, or an outline of the processes of measurement. For a description of these methods the student is referred to any one of the more complete physico-chemical laboratory manuals.*

According to the electro-magnetic theory of light,

$$D = n^2, \qquad (21)$$

where D is the dielectric constant of an insulating medium and n is the index of refraction for electric vibrations of infinite wave-length. Notwithstanding the fact that the foregoing relation is theoretically valid for vibrations of infinite wave-length only, it has been shown by experiment to hold very satisfactorily for vibrations whose wave-lengths range from one to two meters. With substances possessing moderate electric conductivity, it has been found, on measuring the index of refraction for electric vibrations of finite wave-length, that the calculated values of D are not satisfactory. Under these conditions, it is necessary to make allowance for the absorbing power of the medium, and equation (21) becomes,

$$D = n^2(1 - x^2), \qquad (22)$$

where x represents the *absorption index*. In order that the value of x may be calculated, the conductivity and the dielectric constant of the medium and the wave-length of the incident electric vibrations must be known. With normal substances, the absorbing power increases with increase in both the conductivity of the medium and the wave-length of the incident vibrations. Since most organic compounds are poor conductors of electricity, they are found to be practically non-absorbers of all electric vibrations of wave-lengths under one meter. There are some organic compounds, however, which behave exceptionally in this respect, and, notwithstanding the fact that they are practically

* Physico-chemische Messungen (Vierte Auflage) Ostwald-Luther, pp. 557–563.

See also an article on the measurement of dielectric constants by H. Harris, Jour. Chem. Soc., 127, 1049 (1925), in which the author claims to have developed a method for the measurement of this quantity capable of greater accuracy than has heretofore been possible of attainment.

non-conductors, they exhibit marked absorbing power for electric vibrations of comparatively short wave-lengths. With these anomalous absorbers, the value of n^2 is invariably less than the dielectric constant of the medium, and the absorbing power increases with decreasing wave-length of the incident vibrations.

Drude* was the first to point out that, with the exception of water, all compounds containing hydroxyl groups exhibit anomalous electric absorption. He also showed that anomalous electric absorption is conditioned by the dielectric constant of the medium, those compounds which have small dielectric constants being characterized by small absorbing power. While Drude inferred that compounds which do not contain hydroxyl groups are non-absorbers, subsequent investigations render it highly probable that there are other groups beside the hydroxyl group which favor anomalous electric absorption. In general, it may be said that anomalous electric absorption is a constitutive property.

The values of the dielectric constants for some of the more common solvents are given in the accompanying table.

DIELECTRIC CONSTANTS AT 18° C.

Substance.	D
Hydrogen dioxide	92.8
Water	77.0
Formic acid	63.0
Methyl alcohol	33.7
Ethyl alcohol	25.8
Ammonia, liquid	22.0
Chloroform	5.0
Ether	4.35
Carbon tetrachloride	2.25
Benzene	2.28

The importance of this property will become more apparent in subsequent chapters, especially in those devoted to electrochemistry.

* Wied. Ann., 55, 633 (1895); 58, 1 (1896); 59, 17 (1896); 60, 50 (1897); Zeit. phys. Chem., 23, 282 (1897).

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The Relations between Chemical Constitution and Some Physical Properties. Samuel Smiles.
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PROBLEMS

1. Calculate the molecular volume of ethyl butyrate. The molecular volume determined by experiment at the boiling point is 149.1.

2. For propionic acid, $d = 1.0158$ and $n_D = 1.3953$. Calculate the molecular refraction by the formula of Lorenz-Lorentz and compare the value so obtained with that derived from the atomic refractions of the constituent elements.

3. The density of ether is 0.7208, of ethyl alcohol, 0.7935 and of a mixture of ether and alcohol containing p per cent of the latter, 0.7389. At 20° C. the refractive indices for sodium light are, for ether, 1.3536, for alcohol, 1.3619, and for the mixture, 1.3572. Calculate the value of p, using the Gladstone and Dale formula. *Ans.* 20.81.

4. At 20° C. the density of chloroform is 1.4823 and the refractive index for the *D*-line is 1.4472. From the atomic refractivities of carbon and hydrogen given on p. 128, calculate that of chlorine, using the Lorenz-Lorentz formula.

CHAPTER VI

ELEMENTARY PRINCIPLES OF THERMODYNAMICS

Thermodynamics Defined. The science of thermodynamics treats of the laws governing the quantitative transformations of heat energy into other forms of energy. In other words, it is the science of heat considered as a form of energy, and includes the study of the relation of heat energy to all other forms of energy whether mechanical, electrical or chemical. A knowledge of the fundamental principles of thermodynamics is essential to the student of physical chemistry; in fact, thermodynamics constitutes the underlying framework of the entire science of physical chemistry.

Energy. Since thermodynamics deals with energy and its transformations it is essential that the student should have a clear understanding of the meaning of the term "energy." Energy may be defined as the capacity of a body, or system, to perform work. Since the work done affords a measure of the energy expended, it follows that both energy and work are to be measured in terms of the same unit, the *erg*. Energy stored in a system by virtue of its motion is known as *kinetic energy*. This definition applies equally to the motion of the molecules constituting a system and to the motion of the system as a whole. Energy stored in a system by virtue of its position is called *potential energy*. The energy contained in a body by virtue of its temperature and molecular structure, or the sum of its internal kinetic and potential energies, is known as its *intrinsic energy*. Since the deductions of thermodynamics are independent of any molecular hypothesis, we are not so much concerned as to whether the energy of a system is kinetic or potential, as we are to ascertain the gain or loss in energy which the system may experience in undergoing a given transformation.

Although we may employ algebraic symbols to represent the total energy stored in a system, it should be borne in mind that we

possess no means of measuring this energy. When a process occurs in which the energy of a system undergoes change, our measurements merely give us the gain or loss in the energy of the system as a result of the change. For example, let a body having a mass of one gram fall, under the influence of gravity, through a distance of one meter: the resulting loss in potential energy is 1 g. $\times$ 981 cm./sec.^{2} $\times$ 100 cm. = 98,100 ergs. In this calculation, the absolute values of the potential energy of the body in its initial and final states are not involved, and all that we have learned is, that in its final state the body possesses 98,100 ergs less potential energy than it did in its initial state.

All forms of energy may be expressed as the product of two factors, — an "intensity factor" and a "capacity factor." Thus, in the preceding example, potential energy is the product of a force, — the intensity factor, — and a distance, — the capacity factor: or to cite another example, heat energy is the product of temperature, — the intensity factor, — and quantity of heat, — the capacity factor.

The First Law of Thermodynamics. The science of thermodynamics is based upon two fundamental principles known as the first and second laws of thermodynamics.* While the first law is a generalization derived from direct experiments, the second law rests for its verification upon human experience: though less rigorously established, the acceptance of the second law is justified by the fact that no exceptions to it have as yet been found.

The first law is merely a statement of the principle of the conservation of energy, according to which we learn that energy may be changed from one form to another, but that it can never be created or destroyed. This fundamental principle was first clearly formulated by Mayer in 1842, shortly after the publication of the results of the important investigations of Helmholtz, Joule, Hirn and others on the transformation of heat into work and work into heat. These experimenters established the fact that when work is transformed completely into heat, or heat into work, the quantity of work is equivalent to the quantity of heat. Thus, if Q units of heat disappear in any process, and W units of work are produced, then,

* Another principle, originally advanced by Nernst and since confirmed by others, is now commonly referred to as the "Third Law of Thermodynamics." Its consideration lies beyond the scope of this book.

if no other forms of energy are involved, the following relation holds: —

$$W = JQ, \tag{1}$$

where J is a proportionality factor, called the *mechanical equivalent of heat.* The value of the mechanical equivalent of heat as computed from the most reliable sources is $J = 4.183 \times 10^7$ *ergs per gram-calorie.*

Reversible and Irreversible Processes. Any process in which the successive steps of the direct process occur in exactly the reverse order, is called a *reversible* process. A reversible process is to be considered as the ideal limit to which actual processes may approach ever so closely, but never completely attain. Although no natural process is known in which strict reversibility can be fully realized, nevertheless, thermodynamic deductions based upon the assumption of completely reversible processes are perfectly valid.

An *irreversible* process is one in which the successive steps of the direct process cannot be retraced. In such a process the system suffers a permanent loss of energy, in consequence of which, the amount of work performed never attains to the theoretical maximum value.

Reversible and Irreversible Cycles. If after the completion of any process, a system is restored to its initial state, it is said to have undergone a *cycle* of changes, and the process is referred to as a cyclic process. Cycles may be either reversible, or irreversible, according to whether they can be performed in the reverse order or not.

Since after the completion of a reversible cycle, the chemical and physical properties of a system are restored to their original values, it follows that the internal, or total, energy of the system has not undergone any change. It should be pointed out, however, that although the value of the internal energy of the system remains unchanged, heat may be evolved or absorbed, and work may be done, either by, or upon the system during a reversible cyclic process. Since for a completely reversible cycle, $U = 0$, it follows, from the first law of thermodynamics, that $W = Q$, or, if during the cycle there are several operations in which exchanges of heat and work occur, the sum of all the terms involving work, (ΣW), must be equal to the sum of all the terms involving

heat, (ΣQ); that is, $\Sigma W = \Sigma Q$. This equality holds, irrespective of the physical state of the system, whether the cycle be isothermal or nonisothermal. Furthermore, it can be shown that the work done in any reversible, isothermal, cyclic process is zero.

In the application of thermodynamics to the ordinary problems of physics and chemistry, reversible cyclic processes are by far the more important.

If a system undergoes a change which is not cyclic, the initial and final states will be different and the relation between Q and W cannot be expressed *a priori*. If the values of Q and W are known, the two following possibilities exist: — (I) Q may be equal to W, although the process is not cyclic. The expansion of a perfect gas may be cited as an illustration of this case. (II) Q may not be equal to W. If the possibility of extraneous transformations of energy be excluded, it follows from the first law, that

$$Q - W = U_2 - U_1, \tag{2}$$

where U_1 and U_2 denote the internal energies of the system before and after the change. If there are several heat and work terms, equation (2) may be written in the generalized form

$$Q - W = U_2 - U_1 = \Delta U. \tag{3}$$

This equation, it should be observed, affords no information as to the separate values of U_1 and U_2, but merely defines the increase in the internal energy of the system. The terms U_1 and U_2 include the energy due to molecular vibration and attraction, intra-molecular and intra-atomic attraction, together with chemical and other indeterminate forces.

While ΔU is a perfectly definite quantity which is solely dependent upon the initial and final states of the system for any particular process, the values of both Q and W may vary with the experimental conditions. For example, if the process be conducted at constant volume and the factors of mechanical energy alone are involved in the performance of external work, $W = 0$ and consequently $\Delta U = Q$. In other words, the total gain in internal energy is derived from the heat of the environment of the system. As a rule, however, most processes take place at constant pressure rather than at constant volume, and in such cases external work is performed either by, or on, the environment.

Thus, the external work performed by a system on its surroundings will be

$$p(v_2 - v_1) = p\Delta v,$$

where p is the pressure and Δv is the increase in volume of the system. The quantity of heat Q, taken up from the environment, will thus be increased by the amount $p\Delta v$, since

$$Q = \Delta U + W = \Delta U + p\Delta v. \tag{4}$$

If the process be carried out in such a manner that the system neither gains nor loses heat, it is known as an *adiabatic* process. In an adiabatic process, $Q = 0$, and the work performed by the system upon the environment must be derived from the internal energy of the system, or

$$\Delta U = -W. \tag{5}$$

Since ΔU depends solely upon the initial and final states of the system, it follows that dU must be a perfect differential, or

$$dU = \frac{\partial U}{\partial x}dx + \frac{\partial U}{\partial y}dy + \frac{\partial U}{\partial z}dz + \ldots$$

where x, y and z represent such variables as temperature, pressure and volume. While dU is a perfect differential, the same is not true of either Q or W, the values of which are solely dependent upon the path followed by the process.

Heat Content. It has already been shown that when a system undergoes a thermal change, the heat absorbed at constant volume is given by the expression,

$$Q_v = U_2 - U_1 = \Delta U,$$

whereas the heat absorbed at constant pressure is

$$Q_p = (U_2 - U_1) + W = (U_2 - U_1) + p(v_2 - v_1).$$

This equation may be transformed thus:

$$Q_p = (U_2 + pv_2) - (U_1 + pv_1). \tag{6}$$

According to equation (6), the heat absorbed at constant pressure is defined by the initial and final states of the system. If we re-

place $U + pv$ by H, a quantity known as the *heat content* of the system, equation (6) takes the form,

$$Q_p = H_2 - H_1 = \Delta H. \tag{7}$$

In other words, the heat absorbed at constant pressure is the increase in H, while that absorbed at constant volume is the increase in U. It is important to observe that H, like U, is a single-valued function of several variables and that both $dQ_v = d\,U$ and $dQ_p = d\,H$ are perfect differentials.

Heat Capacity. The mean heat capacity, $\bar{c}$, of a system between any two given temperatures may be defined as the quantity of heat required to raise the system from the lower to the higher temperature divided by the difference between the two temperatures, or

$$\bar{c} = \frac{Q}{T_2 - T_1}, \tag{8}$$

where Q is the quantity of heat and T_1 and T_2 are the initial and final temperatures respectively. The true heat capacity at any given temperature may be defined by the differential expression,

$$c = \frac{dQ}{dT}, \tag{9}$$

since the heat capacity varies with the temperature.

It is obvious that the magnitude of the heat capacity of a system will depend upon whether it is determined at constant volume, or at constant pressure. If the heat capacity is determined at constant volume, no external work will be performed and the heat absorbed will be a measure of the increase in the internal energy of the system. The heat capacity at constant volume per mol of substance C_v, is, therefore, defined by the expression,

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v. \tag{10}$$

On the other hand, at constant pressure external work is performed and the heat capacity per mol of substance C_p is defined by the equation,

$$\left(\frac{\partial H}{\qquad}\right) \tag{11}$$

Internal Energy of a Perfect Gas. It has been shown that any two of the three variables, temperature, pressure and volume suffice to define the condition of a gas. The change in the internal energy of a gas may, therefore, be expressed by an equation of the form,

$$dU = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv, \tag{12}$$

where temperature and volume are the chosen variables. The differential coefficient, $\frac{\partial U}{\partial T}$, represents the heat absorbed by a mol of gas when it is heated one degree at constant volume and, therefore, according to equation (10), it may be replaced by C_v. Equation (12) now assumes the form,

$$dU = C_v dT + \frac{\partial U}{\partial v} dv. \tag{13}$$

But according to equation (3)

$$dU = Q - W,$$

and consequently we have

$$Q = C_v dT + \frac{\partial U}{\partial v} dv + W. \tag{14}$$

The work of increasing the volume of a gas by an amount dv at constant pressure, p, is pdv. Hence equation (14) becomes,

$$Q = C_v dT + \frac{\partial U}{\partial v} dv + pdv. \tag{15}$$

The Gay-Lussac-Joule Experiment. In order to determine whether the temperature of a gas undergoes any change when the gas expands into a vacuum, Gay-Lussac, in 1807, carried out the following important experiment. Two large vessels of equal capacity and provided with thermometers, were connected by means of a pipe, fitted with a valve. One vessel was filled with gas, and the other was evacuated. On opening the valve and allowing the gas to expand into the evacuated vessel, the temperature of the gas in the first vessel was observed to fall. A corresponding rise in temperature occurred in the second vessel, due to the compression of its contents. When equilibrium of

pressure had been established, the decrease of temperature in the first vessel was found to be exactly equal to the increase of temperature in the second vessel. From this, Gay-Lussac concluded that, taken as a whole, the gas showed no tendency to become warmer, or colder, during free expansion. A somewhat similar experiment was performed by Joule in 1844. He immersed two similarly connected vessels in a calorimeter, and found that no appreciable change in the temperature of the water of the calorimeter occurred during the free expansion of a gas.

From these two experiments it is evident, that when a perfect gas expands freely into a vacuum, heat is neither evolved nor absorbed. Furthermore, the volume of the system, as a whole, remains constant, and, therefore, no external work is done. Since $Q = 0$ and $W = 0$, in the equation, $U = Q - W$, it follows that $U = 0$, i.e., the *internal energy of a given mass of a gas is independent of the volume.* Subsequent experiments by Joule and Thomson have shown that this statement is only approximately true for actual gases. A slight change in temperature does occur when a gas expands freely, due to the fact that a certain amount of work is required to overcome the mutual attraction of the molecules for each other. For a perfect gas, however, in which no such attractive forces exist, the internal energy is independent of the volume. This phenomenon is known as the Joule-Thomson effect.

The Joule-Thomson Effect. In their investigation of the departure of real gases from ideal behavior, Joule and Thomson conducted a series of important experiments on the thermal effects accompanying gaseous expansion. A continuous current of gas, under a constant pressure higher than that of the atmosphere, was forced through an insulated tube containing a porous plug of cotton or silk. The temperature of the gas was observed both before and after its passage through the plug, and, after introducing several corrections, the true temperature of the gas after expansion was determined. It was found that air, oxygen, nitrogen and carbon dioxide were all cooled by expansion, while with hydrogen a slight rise in temperature was found to occur. The essential features of the experiment are represented diagrammatically in Fig. 60 in which P is the porous plug and A and B are two movable pistons. The work done in forcing a mol of gas at volume v_1 and pressure p_1 through the plug is p_1v_1. Similarly,

on the opposite side of the plug, the work done by the gas in driving B outward against atmospheric pressure is p_2v_2. If the behavior of the gas is not ideal, external work will be performed by the system as a whole, and we may write

$$p_2v_2 - p_1v_1 = W.$$

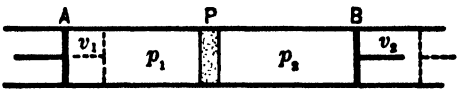

Fig. 60

If the system is thermally insulated and the process is adiabatic, $Q = 0$, and we have, according to equation (3),

$$\Delta U = U_2 - U_1 = -W = p_1v_1 - p_2v_2,$$

or $$U_2 + p_2v_2 = U_1 + p_1v_1.$$

But $$U_2 + p_2v_2 = H_2, \quad \text{and} \quad U_1 + p_1v_1 = H_1,$$

hence $$H_2 = H_1.$$

It is apparent, therefore, that in the free expansion of a real gas, the heat content or enthalpy, and not the internal energy, remains constant. In consequence of this fact, the Joule-Thomson effect may be defined mathematically by the expression,

$$k = \left(\frac{\partial T}{\partial p}\right)_H. \tag{16}$$

Since H is a single-valued function of any two of the three variables T, p and v, we may write

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp.$$

But in the case of the free expansion of a real gas, H is constant, or $dH = 0$.

Hence,

$$\frac{dT}{dp} = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{C_p}. \tag{17}$$

It should be observed that the Joule-Thomson coefficient is determined by the variation, at constant temperature, of the heat content H of the gas with the pressure p.

With the exception of hydrogen and helium, it has been found that if the pressure be increased isothermally, the product pv at first decreases and then increases. Hence, for moderate pressures, the product p_2v_2 will be greater than the product p_1v_1, and the net external work performed by the gas upon the environment will be positive for all gases except hydrogen and helium. If the expansion be conducted adiabatically, the temperature of the system will be lowered. At higher pressures, on the other hand, the product p_2v_2 is observed to be less than the product p_1v_1 and the temperature of the system rises with the passage of the gas through the porous plug. When a real gas expands adiabatically, the force of inter-molecular attraction is overcome at the expense of the kinetic energy of the molecules and a corresponding decrease in temperature follows. It appears, therefore, that the heating or cooling effect observed when a gas expands through a porous plug is really the resultant of two separate effects which are due to different causes.

These two component effects must operate in such a manner that the value of H shall remain constant throughout the process.

Rose-Innes* discovered that the experimental data of Joule and Thomson could be satisfactorily represented by the equation,

$$\frac{dT}{dp} = \frac{a}{T} + b, \tag{18}$$

where a and b are empirical constants. In the case of carbon dioxide and air, the values of both a and b were found to be positive, while in the case of hydrogen, the value of b was negative. Thus, for hydrogen, $a = 64.1$ and $b = -0.331$; on substituting these values in the Rose-Innes equation, it is found that $dT/dp = 0$ when $t = -79°$ C. or 194° abs. Above $-79°$, dT/dp is negative while at lower temperatures dT/dp is positive. The temperature at which the sign of the differential coefficient, dT/dp, undergoes reversal is known as the *inversion temperature*.

Both temperature and pressure exert an influence on the magnitude of the Joule-Thomson coefficient. An increase in pressure,

* Rose-Innes, Phil. Mag., 45, 227 (1898).

or a decrease in temperature, causes a diminution in the value of dT/dp. While the effect of pressure has thus far only been formulated empirically, it has been found that the influence of temperature can be accurately summarized by the generalization, that *the value of the Joule-Thomson coefficient varies inversely as the square of the absolute temperature.*

As has already been pointed out, the Joule-Thomson effect finds practical application in the apparatus developed by Linde and Claude for the liquefaction of gases (see p. 68).

Relation between the Two Specific Heats, C_p and C_v. It has already been proven that

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad \text{and} \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_v.$$

Therefore,
$$\begin{aligned} C_p - C_v &= \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v, \\ &= \left[\frac{\partial (U + pv)}{\partial T}\right]_p - \left(\frac{\partial U}{\partial T}\right)_v, \\ &= \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v. \end{aligned} \tag{19}$$

But since U is a single-valued function of the variables T and v, it follows that

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial v}\right)_T dv,$$

and therefore,

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p.$$

Substituting in equation (19) we obtain

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v. \tag{20}$$

But for a perfect gas, $\left(\frac{\partial U}{\partial v}\right)_T = 0.$

Hence equation (20) becomes

$$C_p - C_v = p\left(\frac{\partial v}{\partial T}\right)_p, \tag{21}$$

and since $pv = RT$, we may replace $\left(\frac{\partial v}{\partial T}\right)_p$ by R/p, and equation (21) then simplifies to

$$C_p - C_v = R, \tag{22}$$

an expression which has already been derived in connection with the kinetic theory of gases (see p. 47).

Isothermal and Adiabatic Expansion. When a gas expands, its temperature will fall, unless an amount of heat is supplied from its surroundings sufficient to compensate for the energy expended in the performance of external work. When this natural tendency of a gas to undergo cooling during free expansion is thus offset, and the temperature of the gas remains constant, the gas is said to expand *isothermally*.

When the temperature of a gas is maintained constant, by supplying heat during expansion, or abstracting heat during compression, the process is known as an isothermal process. On the other hand, when a gas undergoes expansion or compression, and it neither receives heat from, nor imparts heat to its surroundings, the process is known as an adiabatic process. If a gas be compressed adiabatically, the temperature rises and tends to cause the gas to expand; this temperature effect opposes the compressing force, and therefore, more work is required to bring about a given change in volume by adiabatic compression than by isothermal compression. This becomes clear if we make use of the diagram shown in Fig. 61, in which pressures are plotted as ordinates, and volumes as abscissas. If a gas be compressed isothermally from volume v_1 to volume v_2, the work done will be represented by the area ABv_2v_1, whereas if it be compressed adiabatically, the work done will be represented by the area ACv_2v_1. It will be noticed that the slope of the adiabatic line, AC, is steeper than that of the isothermal line, AB.

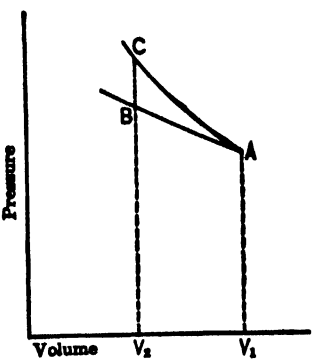

Fig. 61

Since for a perfect gas, $\left(\frac{\partial U}{\partial v}\right)_T = 0$, it follows that the equation

formulating the first law of thermodynamics,

$$\Delta U = Q - W,$$

becomes, in the case of isothermal expansion,

$$Q = W.$$

Now if the gas be allowed to expand by an infinitesimal amount dv, under a pressure p, the work performed will be pdv, and we shall have

$$Q = pdv.$$

For a finite increment in volume from v_1 to v_2,

$$Q = \int_{v_1}^{v_2} pdv.$$

Since for one mol of gas, $pv = RT$, it follows that

$$Q = RT\int_{v_1}^{v_2}\frac{dv}{v} = RT\ln\frac{v_2}{v_1}. \tag{23}$$

But $p_1v_1 = p_2v_2$, where p_1 and p_2 are the pressures corresponding to v_1 and v_2 respectively, hence

$$Q = RT\ln\frac{p_1}{p_2}. \tag{24}$$

In the adiabatic expansion of a perfect gas, $Q = 0$, and the fundamental equation,

$$\Delta U = Q - W,$$

reduces to

$$\Delta U = -W = -p\Delta v.$$

But $dU = C_v dT$ (equation 10), hence

$$C_v dT = -pdv.$$

Since for one mol of gas, $pv = RT$, it follows that

$$C_v dT = -RT\frac{dv}{v}.$$

But $R = C_p - C_v$ (equation 22), hence

$$C_v dT = -(C_p - C_v)T\frac{dv}{v}.$$

Dividing both sides of the equation by $C_v T$, and denoting the ratio of the two specific heats, C_p/C_v, by γ, we have

$$\frac{dT}{T} = -(\gamma - 1)\frac{dv}{v}.$$

If v_1 is the initial volume of the gas at the temperature T_1, and v_2 is the final volume at the temperature T_2, we have, on integrating,

$$\int_{T_1}^{T_1} \frac{dT}{T} = (\gamma - 1)\int_{v_1}^{v_1} \frac{dv}{v},$$

whence $$\ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{v_1}{v_2},$$

or $$T_1 v_1^{\gamma - 1} = T_2 v_2^{\gamma - 1}. \tag{25}$$

Since $p_1 v_1 = RT_1$ and $p_2 v_2 = RT_2$, it follows that

$$p_1 v_1^{\gamma} = p_2 v_2^{\gamma}, \tag{26}$$

or $$p_1^{1-\gamma} T_1 = p_2^{1-\gamma} T_2. \tag{27}$$

Carnot's Cycle. In establishing the law which determines the maximum quantity of heat which can be converted into work, Carnot made use of an imaginary engine, which was caused to perform a reversible cycle of operations, consisting of two isothermal and two adiabatic volume changes. Such a cycle of operations is shown in the accompanying diagram (Fig. 62), and is known as a *Carnot cycle*. The four successive steps involved in the completion of the cycle may be conveniently considered in the following order:—

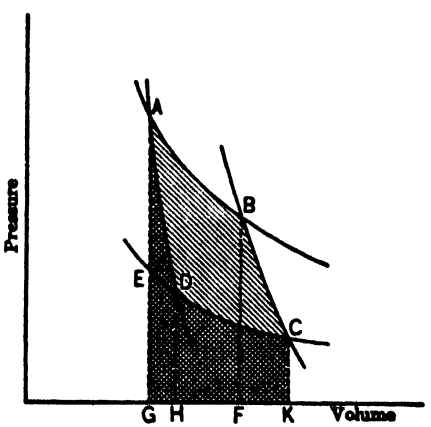

Fig. 62

(1) Let A represent the initial state of the system, and let us suppose that it expands isothermally at the temperature T, along AB, through an infinitely small volume dv. During the expansion, a quantity of heat Q will be withdrawn from the surroundings, and a quantity

of work represented by the area, $ABFG$, will be done by the system.

(2) The system is next allowed to expand adiabatically along BC, with an accompanying fall in temperature dT. The work done in this stage of the process is represented by the area, $BCKF$.

(3) The system is now compressed isothermally at the temperature $T - dT$, along CD, with an evolution of a quantity of heat Q', slightly less than Q. The work done upon the system in this stage is represented by the area, $CDHK$.

(4) Finally the system is compressed adiabatically along DA, the temperature rising until the initial temperature is attained, and the system is restored to its original condition. The work done on the system during the last stages is represented by the area, $DAGH$.

The net work done by the system is represented by the area, $ABCD$, as will be evident from the diagram, in which the areas representing work done *by* the system are shaded from left to right, while the areas representing work done *upon* the system are shaded from right to left. According to the first law of thermodynamics, the net work done in the cycle must be equivalent to the heat lost, $Q - Q'$.

Carnot's cycle is the only completely reversible process by which an indefinite amount of work can be performed between a source and a condenser, each of which is maintained at a constant temperature.

The ratio of the quantity of work produced by a heat engine, to the quantity of heat absorbed from the source, is known as the *efficiency* of the engine. Since the net work done in the completion of a Carnot cycle is equivalent to $Q - Q'$, it follows that the efficiency of an engine performing such a cycle will be given by the expression, $\frac{Q - Q'}{Q} = \epsilon$.

It may be readily shown, that of all heat engines working between two given temperatures, that which is perfectly reversible has the maximum efficiency and, furthermore, that all reversible heat engines working between the same two temperatures have the same efficiency.

The Second Law of Thermodynamics. Attention has already been directed to the fact, that although work can always be transformed into heat, this is not equally true of the reverse process, —

the transformation of heat into work. The first law of thermodynamics merely specifies, that when heat is converted into work, a definite quantitative relationship exists between the heat absorbed and the work done, but it tells us absolutely nothing as to the amount of work which can be obtained from a given quantity of heat. It is to the second law of thermodynamics that we must turn for information as to the limitations which experience has shown govern the transformation of heat into work. The second law, as stated by Clausius, is as follows: — "*It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.* In other words, heat cannot of itself pass from a colder to a hotter body, but tends invariably toward a lower thermal level. It should be clearly understood that this is in no way contradictory to the first law. The first law is concerned solely with the quantitative relationship governing the transformation of heat into work: it does not affirm that such transformations are possible under all conditions.

Maximum Work. Let us consider the isothermal expansion of one mol of a perfect gas enclosed in a cylinder fitted with a frictionless and weightless piston. In order that the gas may perform a maximum amount of work in expanding through an infinitely small volume, dv, it is necessary that the external pressure on the piston shall be less than the pressure of the gas, p, by an infinitely small amount, dp. Under these conditions, the effective pressure to be overcome by the gas in expanding is $(p - dp)$, while the work done will be $(p - dp)dv = pdv$, the product, $dp.dv$, being an infinitely small quantity of the second order. If the external pressure is just equal to the gas pressure, obviously the piston will remain stationary, and no work will be done. If, however, the value of the external pressure be increased so as to exceed the pressure of the gas by dp, the effective pressure on the piston will be $(p + dp)$ and an amount of work $-(p + dp)dv = -pdv$, will be done *upon* the gas, the negative sign indicating that the volume of the gas is decreasing. It follows, therefore, that the numerical value of the work performed by the gas expanding isothermally against a pressure $(p - dp)$, is equal to the numerical value of the work performed upon the gas by a pressure $(p + dp)$. Such a process is said to be *reversible.*

If instead of expanding through an infinitely small volume, dv,

the gas be allowed to undergo an appreciable expansion, say from volume v_1 to volume v_2, the pressure of the gas cannot be taken as a constant quantity, since, according to Boyle's law, the pressure varies inversely as the volume. The expression $p(v_2 - v_1)$, therefore, no longer holds for the maximum work done by the gas. In order to calculate the maximum work done by a gas in expanding isothermally through a measurable volume, the total expansion from volume v_1 to volume v_2, must be treated as the sum of a series of infinitely small expansions in each of which the increment of volume, dv, is multiplied by the value of the pressure corresponding. The maximum work, W, will then be expressed by the equation,

$$W = \int_{v_1}^{v_2} p dv.$$

Since for a perfect gas, $pv = RT$, or $p = RT/v$, we have

$$W = RT \int_{v_1}^{v_2} \frac{dv}{v}.$$

Integrating, we obtain

$$W = RT \ln \frac{v_2}{v_1}. \tag{28}$$

But $v_1 = RT/p_1$ and $v_2 = RT/p_2$, hence equation (28) takes the form,

$$W = RT \ln \frac{p_1}{p_2}. \tag{29}$$

Equation (28) is an expression for the maximum work performed by one mol of gas in expanding, isothermally and reversibly, from volume v_1 to volume v_2. Equation (29) is a similar expression involving pressure instead of volume.

It should be pointed out that a characteristic of every ideal reversible process is that the external work done by the system is the maximum amount of work which the system is capable of performing.

In an adiabatic expansion, $Q = 0$, and the equation expressing the first law of thermodynamics becomes

$$\Delta U = -W.$$

Since $dU = C_v dT$, it follows that the maximum work derivable from an adiabatic expansion will be

$$C_v(T_2 - T_1) = \int_{v_1}^{v_2} p dv. \tag{30}$$

In a complete Carnot cycle, therefore, where all of the operations are conducted reversibly, the external work performed is the maximum amount of work which the system can accomplish, and consequently

$$W = Q_2 \frac{T_2 - T_1}{T_2}, \tag{31}$$

where Q_2 is the quantity of heat transferred from temperature T_2 to temperature T_1. In all actual processes the amount of external work obtainable will of course be less than the theoretical amount calculated by means of equation (31).

Mathematical Formulation of the Second Law. A mathematical expression of the second law can be derived from a consideration of the behavior of a perfect gas undergoing a reversible cycle of changes. Let us imagine one mol of a perfect gas, the volume of which is v_1 at the temperature T, to be enclosed in a cylinder fitted with a frictionless and weightless piston. Let the gas expand isothermally, from the volume v_1 to the volume v_2. In this expansion, the maximum work which the gas can perform is, according to equation (23),

$$W = RT \ln \frac{v_2}{v_1}. \tag{32}$$

Since the change in internal energy, U, of a perfect gas depends only on the temperature, it follows that $U = 0$, if the gas expands isothermally. According to the first law,

$$U = Q - W,$$

but $U = 0$ and consequently $W = Q$. Substituting this value of W in equation (32), we have

$$W = Q = RT \ln \frac{v_2}{v_1}, \tag{33}$$

or

$$\frac{Q}{T} = R \ln \frac{v_2}{v_1}. \tag{34}$$

It is of importance to observe that while W, in the foregoing equations, represents the maximum work which can be done by a gas in expanding isothermally from volume v_1, to volume v_2, it by no means implies that such a maximum value must necessarily be attained. For example, in the experiment of Gay-Lussac on the expansion of a gas into a vacuum, the value of W is always zero. The value of $RT \ln \frac{v_2}{v_1}$, on the other hand, is a maximum value. Thus, if we compress the gas isothermally, until the original volume, v_1, is restored, the work involved under ideal conditions must, at least, be equal to W. Therefore, the maximum work obtainable with a perfect engine must be that corresponding to a reversible process. Let the foregoing operations be repeated at a higher temperature, $T + dT$. The maximum work done will be

$$W + dW = R(T + dT) \ln \frac{v_2}{v_1}. \tag{35}$$

On subtracting equation (33) from equation (35), we obtain

$$dW = RdT \ln \frac{v_2}{v_1}. \tag{36}$$

But according to equation (34),

$$R \ln \frac{v_2}{v_1} = \frac{Q}{T},$$

therefore, we have

$$dW = Q \frac{dT}{T}. \tag{37}$$

This is the mathematical expression of the second law of thermodynamics.

It should be borne in mind, that equation (37) holds only for a reversible cycle. If the cycle is irreversible, the amount of work obtainable will be less than that given by the equation. Hence, for irreversible processes we have the inequality,

$$dW < Q \frac{dT}{T}. \tag{38}$$

Equation (37) can be transformed as follows: —

$$Q = T\left(\frac{\partial W}{\partial T}\right)_v, \tag{39}$$

where the partial differential coefficient denotes the rate of change in the maximum work with the absolute temperature, at constant volume. This is a convenient form in which to use the equation expressing the second law of thermodynamics.

The Equation of Clapeyron. It may be proven geometrically that the area, $ABCD$, in Fig. 62 is equal to the product of EA and GF. From the diagram it is evident, that AE represents the increase in pressure corresponding to an increase in temperature dT, when the system is maintained at constant volume. Expressing this mathematically, we have

$$AE = \left(\frac{\partial p}{\partial T}\right)_v dT.$$

In like manner, FG will be seen to represent the small increase in volume, dv. Therefore, since the net work done in performing the cycle is represented by the area $ABCD$, we have

$$dW = \left(\frac{\partial p}{\partial T}\right)_v dT.dv. \tag{40}$$

But, as has already been proved (see equation 37),

$$dW = Q\frac{dT}{T},$$

in which Q denotes the heat absorbed in a reversible cycle. In the cycle we are now considering, the quantity of heat withdrawn from the source may be expressed by the partial differential coefficient, $\left(\frac{\partial Q}{\partial v}\right)_T dv$: therefore, equation (40) becomes

$$\left(\frac{\partial p}{\partial T}\right)_v dT.dv = \left(\frac{\partial Q}{\partial v}\right)_T dv.\frac{dT}{T},$$

or

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial Q}{\partial v}\right)_T. \tag{41}$$

The differential coefficient, $\left(\frac{\partial Q}{\partial v}\right)_T$, may be interpreted as the quantity of heat which must be added to the system in order that its temperature may remain constant during unit increase in volume. This is called the " latent heat of expansion," and is related to

the term "latent heat" as usually defined in the following manner: — Let v_1 and v_2 denote the volumes of one gram of a given substance in the liquid and vapor stages respectively, and let L be its latent heat, i.e., the quantity of heat required to transform one gram of the substance from the liquid to the vapor state, it is evident that

$$\frac{L}{v_2 - v_1} = l,$$

where l is the latent heat of expansion. Therefore, equation (41) becomes,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial Q}{\partial v}\right)_T = \frac{l}{T} = \frac{L}{T(v_2 - v_1)}. \tag{42}$$

Since the pressure of a saturated vapor is independent of its volume, provided the liquid phase is present, the partial differential coefficient may be replaced by the total differential coefficient, and equation (42) becomes,

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}. \tag{43}$$

This is the well-known equation of Clapeyron. It is of value in the application of thermodynamics to processes involving a change of state. For example, it enables one to calculate the heat of vaporization of a liquid, provided the specific volumes of the liquid and vapor phases, together with the rate of change of the vapor pressure with the temperature, are known.

As an illustration of the use of equation (43), let us calculate the heat of vaporization of water at its boiling-point from the following data: — The vapor pressure of water is 746.52 mm. at 99.5° and 773.68 mm. at 100.5°; the specific volume of water vapor at 100° is 1650.8 cc., and the specific volume of liquid water at 100° is 1.04 cc. Therefore, the value of dp/dT at 100° will be, $773.68 - 746.52 = 2.716$ cm., or $2.716 \times 13.6 \times 981 = 36{,}239$ dynes/cm.^{2}. Substituting the above values in equation (43), we have

$$L = 36{,}239 \times 373\ (1{,}650.8 - 1.04)$$
$$= 22.3 \times 10^9 \text{ ergs.}$$

On dividing this quantity by the mechanical equivalent of heat, $J = 4.183 \times 10^7$ ergs, we obtain $L = 533.1$ calories per gram, as the heat of vaporization of water.

In like manner, the equation may also be applied to the process of fusion. For example, let us calculate the change in the freezing-point of water due to an increase in pressure of one atmosphere. The specific volume of water at 0° is 1.000 cc., and the specific volume of ice at the same temperature is 1.092 cc.: hence, $v_2 - v_1 = 1.000 - 1.092 = -0.092$ cc. The heat of fusion of ice is 79.6 calories per gram, or $79.6 \times 4.183 \times 10^7$ ergs per gram. Substituting in equation (43), we have

$$\frac{dp}{dT} = \frac{79.6 \times 4.183 \times 10^7}{273 \times (-0.092)} = -1.33 \times 10^8 \text{ dynes/cm.}^2$$

That is, 1.33×10^8 dynes/cm.^{2}, is the pressure required to lower the freezing-point of water 1°; therefore, its reciprocal,

$$-\frac{dT}{dp} = \frac{1}{1.33 \times 10^8} = 0.75 \times 10^{-8},$$

will be the lowering in the freezing-point in degrees produced by an increase in pressure of one dyne, and, since one atmosphere is equivalent approximately to 1×10^6 dynes, it follows that the lowering in the freezing-point of water produced by an increase in pressure of one atmosphere will be, $0.75 \times 10^{-8} \times 10^6 = 0.0075°$. The negative sign indicates that increase of pressure lowers the freezing-point; this is due to the fact, that the specific volume of ice is greater than the specific volume of water at the freezing temperature.

The Equation of Clausius-Clapeyron. If we assume that the gas laws apply to vapors, as we may under ordinary conditions, and if we regard the specific volume of a substance in the liquid state as negligible in comparison with the specific volume of its vapor, we may substitute, RT/p, for v_2 in the equation of Clapeyron, and obtain the equation,

$$\frac{dp}{dT} = \frac{\lambda p}{RT^2}. \tag{44}$$

On rearrangement this becomes,

$$\frac{1}{dT} \cdot \frac{dp}{p} = \frac{\lambda}{RT^2},$$

where $\lambda = ML$,

or

$$\frac{d \ln p}{dT} = \frac{\lambda}{RT^2}. \tag{45}$$

Equation (45) is commonly known as the equation of Clausius-Clapeyron, and, together with equation (43), is one of the most useful equations in the science of thermodynamics.

Entropy. The maximum amount of work obtainable from an ideal heat engine operating in a reversible cycle between the temperatures T_1 and T_2, has been shown to be $\frac{Q(T_1 - T_2)}{T_1}$, where Q denotes the quantity of heat delivered to the engine. Expanding this expression, we have

$$\frac{Q(T_1 - T_2)}{T_1} = Q\left(\frac{T_1}{T_1}\right) - Q\left(\frac{T_2}{T_1}\right) = Q - \left(\frac{Q}{T_1}\right)T_2.$$

In this equation, the term, $\left(\frac{Q}{T_1}\right)T_2$, represents the quantity of heat which is not convertible into work, or, in other words, it represents the *unavailable* energy. It is obvious that the unavailable energy will become zero when $T_2 = 0$. Hence, if the temperature of the condenser could be reduced to the absolute zero, the available energy would be represented by Q, and the efficiency of the engine would become 100 per cent.

The quantity $\frac{Q}{T_1} = S$, is called the *entropy* of the system and, like the quantities, U and W, its value is wholly dependent upon the state of the system, and not upon the path by which that state is reached. We may define entropy as that quantity which multiplied by the lowest available temperature gives the unavailable energy. Although the total entropy of a system cannot be measured, it is possible to determine the difference in entropy between two given states. Therefore, entropy is always expressed as an increase, or a decrease, above or below some arbitrarily chosen standard. Since during an adiabatic change, no heat enters or leaves a system, it follows that $dQ = 0$, or $dQ/T = 0$, and therefore, Q/T is constant. Hence, an adiabatic may be regarded as a line of constant entropy. It is on account of this property, that adiabatic lines are frequently called *isentropic* lines. Since adiabatic lines are lines of constant entropy, it is customary in measuring the entropy of a system, to select some one adiabatic, as a reference line, to which all other adiabatics of the system may be referred. The pressure-volume diagram of a given mass of a substance may be ruled off into a series of adiabatic lines, repre-

senting successive states of the substance which differ by definite units of entropy, in just the same manner as the states represented by the isothermal lines differ by definite units of temperature.

Since, in every physical or chemical process occurring in nature, transference of heat is accompanied by a fall in temperature, it follows that, Q/T, must undergo a corresponding increase. In other words, in an *irreversible* process, the entropy tends toward a maximum. When this maximum is reached, the available energy will be zero, and the component parts of the system will all be at the same temperature.

In an *isothermal* reversible process, $\frac{dQ}{T}$ will have a finite value and the increase in entropy, in passing from a state A to a state B, will be represented by the equation,

$$S_B - S_A = \int_A^B \frac{dQ}{T} = \frac{Q}{T}, \tag{46}$$

but

$$\frac{Q}{T} = \frac{dW}{dT}, \qquad \text{(See equation 37)}$$

therefore,

$$S_B - S_A = \frac{dW}{dT}. \tag{47}$$

Change of Entropy in a Perfect Gas. According to the first law of thermodynamics, the heat absorbed by a perfect gas for an infinitesimal change is

$$Q = dU + pdv.$$

But $dS = Q/T$, hence it follows that

$$dS = \frac{dU + pdv}{T},$$

$$= \frac{C_v dT + pdv}{T}. \tag{48}$$

Integrating, on the assumption that C_v is independent of temperature, we have

$$\int dS = C_v \int \frac{dT}{T} + R \int \frac{dv}{v} + \text{const.},$$

or

$$S = C_v \ln T + R \ln v + \text{const.} \tag{49}$$

If one mol of gas expands isothermally from volume v_1 to volume v_2, the change in entropy will be

$$S_2 - S_1 = R \ln \frac{v_2}{v_1}. \tag{50}$$

Change of Entropy with Temperature. If dT is the infinitesimal increase in the temperature of a system, whose heat capacity is C, due to the absorption of a quantity of heat Q, then

$$Q = CdT.$$

But according to equation (46), $dS = Q/T$, therefore

$$dS = C\frac{dT}{T}. \tag{51}$$

According to whether the system is heated at constant volume or constant pressure, we will have

$$dS = C_v\frac{dT}{T} = C_v d \ln T, \tag{52}$$

or

$$dS = C_p\frac{dT}{T} = C_p d \ln T. \tag{53}$$

As an example of the application of these equations we may take the case of liquid mercury between the absolute temperatures $T_1 = 298.1$ and $T_2 = 234.1$. Over this range of temperature C_p may be assumed to remain constant and equal to 6.7 (law of Dulong and Petit). Hence

$$S_1 - S_2 = 2.303 \times 6.7 \log \frac{298.1}{234.1} = 1.62.$$

Change of Entropy in Physical Processes. As has been pointed out, when a system absorbs heat in a reversible process, the increase in the entropy of the system is expressed by the equation,

$$dS = \frac{Q}{T}.$$

This equation may be employed to calculate the change in entropy occurring in both physical and chemical processes. The following example will serve to illustrate the application of the foregoing equation to the calculation of the change of entropy ac-

companying the fusion of mercury at its melting-point, 234°.1 Abs. At this temperature, the two phases, solid and liquid mercury, are in equilibrium and the transition from one state to the other is strictly reversible, the direction of the change being conditioned by temperature and pressure. The heat of fusion of mercury is 560 cal. per mol and, since the temperature remains constant during fusion, we have

$$\Delta S = \frac{\Delta Q}{T},$$

or

$$\Delta S_{234.1} = \frac{560}{234.1} = 2.39 \text{ cal. per degree.}$$

In this process, one mol of mercury has undergone transformation from the solid to the liquid state, hence we may say that the molal entropy of liquid mercury exceeds that of solid mercury by 2.39 units.

Free Energy. Another thermodynamic tool which has proven to be quite as useful to the chemist as the concept of entropy in dealing with various problems of chemical change is the quantity known as *free energy*. In order that a system may do work at constant temperature, energy must be derived, either from the system itself, or else from its surroundings. This energy is known as *available* energy. In other words, it is by no means necessary that a difference in temperature shall exist in order to obtain part of the internal energy of a system in the form of useful work. Thus, in the isothermal expansion of a gas, an unlimited amount of work may be obtained. In this case work is performed at the expense of the heat absorbed by the gas from its surroundings. In order to repeat the process, the gas must again be compressed to its initial volume by performing upon it an amount of work equal to that derived from its expansion with the development of an equivalent amount of heat. The maximum external work done by an isothermal process is generally called the *free energy* of the process.

It is very important to distinguish between the expressions, " change in free energy " and " change in total, or internal, energy," since it is only under special conditions that the two expressions are synonymous. Thus, certain processes are known in which the loss in free energy may exceed the loss in total energy, and other processes are known in which there may be an actual gain

in total energy accompanying a loss in free energy. The exact quantitative relations which connect the change in free energy with the corresponding change in the total, or internal, energy associated with any reversible process, is given by the Gibbs-Helmholtz equation.

If we combine the equation formulating the first law of thermodynamics,

$$U = Q - W,$$

with that expressing the second law,

$$Q = T\left(\frac{\partial W}{\partial T}\right)_v,$$

we obtain

$$Q = W + U = T\left(\frac{\partial W}{\partial T}\right)_v. \tag{54}$$

This is the Gibbs-Helmholtz equation. It is one of the most important formulas in thermodynamics, and finds numerous applications in the domain of physical chemistry.

In certain processes, such, for example, as that occurring in the Daniell cell, the change in free energy with the temperature is practically zero; i.e., $\left(\frac{\partial W}{\partial T}\right)_v = 0$, and consequently $U = -W$. In other words, the change in free energy and the change in total energy are numerically equal, when the temperature coefficient of free energy is zero. It has already been pointed out, that when a process occurs without alteration in volume, the equation expressing the first law, viz.,

$$U = Q - W,$$

takes the form

$$U = Q_v,$$

where Q_v denotes the heat absorbed at constant volume. If this value of U be substituted in equation (54), we obtain

$$W + Q_v = T\left(\frac{\partial W}{\partial T}\right)_v, \tag{55}$$

which is a useful modification of the Gibbs-Helmholtz equation.

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PROBLEMS

1. A piston whose diameter is 20 cm. moves 10 cm. under a pressure of 10 atmospheres. How many calories of heat are transformed into work?

2. In a certain thermodynamic process the system gains 600 calories of internal energy, and at the same time 1200×10^7 ergs of work are done; how much heat must be supplied? What is the efficiency of the process?

3. How many ergs are equivalent to 5 calories?

4. One mol of hydrogen is heated from 0° to 100° C., under a pressure of 1 atmosphere; calculate the increase in the heat content of the gas. Assuming that hydrogen behaves as a perfect gas, calculate the increase in its internal energy. The value of the specific heat at constant pressure $c_p = 3.70$. *Ans.* 740 cal.; 542 cal.

5. A Carnot engine takes in 100 calories and gives out 80 calories. How many ergs of work are done, and what is the efficiency of the engine?

6. A Carnot engine, when reversed, delivers 150 calories to the source. If 300×10^7 ergs are expended, calculate the amount of heat taken from the condenser.

7. How much work, expressed in ergs, can an ideal engine perform, working between the temperatures of 150° and 20°, provided 180 calories are delivered to the engine at the higher temperature? Also calculate the efficiency of the operation.

8. The density of solid phenol is 1.072, and the density of liquid phenol is 1.0561; its heat of fusion is 24.93 calories per gram, and its freezing-point is 34°. Find the change in the freezing-point produced by an increase in pressure of 1 atmosphere.

9. Acetic acid melts at 16.6°, $dT/dp = 0.0242°$ per atmosphere, and the heat of fusion is 46.42 calories per gram. Calculate the change in volume accompanying the liquefaction of 1 gram of acid.

10. From the following data calculate the value of dp/dT for ethyl propionate: — density in liquid state, 0.7958, density in vapor state, 0.0033, both of the foregoing values corresponding to the boiling-point of ethyl propionate, 99°; the heat of vaporization is 77 calories per gram.

11. The heat of vaporization of ether is 88.39 calories per gram at 34.5°. Calculate the change in boiling-point due to a change in pressure from 760 mm. to 750 mm.

(NOTE. In equation (44) let $R = 2$ calories, and replace L, the heat of vaporization per gram, by $\lambda = LM$, the heat of vaporization per gram-molecular weight, M.)

12. Compute the heat of vaporization of ethyl formate from the following data: — $dp/dT = 27$ mm., the boiling-point is 54.3° at 760 mm., and the molecular weight is 74.

13. The heat of fusion of ice is 80 calories per gram, and the heat of vaporization of water is 597 calories per gram at the same temperature, viz., 0°. What is the heat of sublimation of ice at 0°?

(NOTE. It follows from the first law of thermodynamics that the heat of sublimation at the freezing-point must be equal to the sum of the heats of fusion and vaporization, i.e., it is immaterial, so far as the expenditure of energy is concerned, whether a substance passes directly from the solid to the gaseous state, or whether it passes first into the liquid state and then into the gaseous state.)

14. The vapor pressure of both ice and water at 0° is 4.62 mm., and the heat of fusion of ice is 80 calories per gram. Calculate the difference between the temperature coefficients of vapor pressure for the two states.

15. Calculate the heat of sublimation of ice from the data of the preceding problem, together with the following data: — The specific volumes of saturated water vapor and ice are 210,680 cc. per gram and 1.092 cc. per gram, respectively, at the vapor pressure 4.619 mm., and the change in vapor pressure per degree is 0.3852 mm.

16. Calculate the lowering of the freezing-point of ice when it is subjected to a pressure of 60 atmospheres. Make use of data given in preceding problems.

17. Calculate the boiling point of water under a pressure of 787 mm. of mercury, having given the following data: — Heat of vaporization of water at 100° C. = 536 cal., boiling point under 760 mm. pressure = 100° C.

Ans. 101.02° C.

18. Compute the temperature at which water should boil at Quito where the average barometer reading is 524.5 mm., assuming that water vapor follows the gas laws. *Ans.* 91.1° C.

19. The boiling point of benzene is 80.36° C. at 760 mm. pressure; its heat of vaporization at the boiling point is 93.45 cal. Find its boiling point when the barometer reads 755.4 mm. *Ans.* 80.15° C.

20. A substance changes state at 80° by the addition of 500 calories. What is the gain in entropy?

21. A system at 80° receives 100 calories. At 60° it rejects 75 calories. What has been the gain in entropy?

22. Compute the increase in entropy when 1 mol of bromine is transformed from the solid state at its melting point, 7.32° C., to vapor at its boiling point, 61.55° C., having given the following data: — Specific heat of liquid bromine, 0.107, heat of fusion 16.185 cal., and heat of vaporization, 43.69 cal. *Ans.* 3456 cal. per degree.

23. Calculate the change in free energy when one gram-molecule of a liquid is evaporated at constant temperature T, and constant pressure p, if v_1 and v_2 are the volumes of one gram-molecule of the liquid and vapor respectively. For water, when $T = 373$, $p = 1$ atmosphere, $v_1 = 18.02$ cc. and $v_2 = 18.02 \times 1674$ cc. Express your answer in calories.

24. Calculate the change in free energy of a system under atmospheric pressure and at 20°, when its internal energy increases by 500 calories; its volume changes from 2 to 5 liters, and its entropy gains 2 units.

CHAPTER VII

SOLUTIONS

Definition of Terms. Having dealt with the properties of pure substances in the gaseous, liquid and solid states we now proceed to the consideration of the properties of mixtures of two or more pure substances. When such a mixture is chemically and physically homogeneous, and no abrupt change in its properties results from an alteration of the proportions of the components of the mixture, it is termed a *solution.*

A solution may also be defined as a homogeneous phase composed of two or more molecular species. Thus, when alcohol is added to water, we obtain, when equilibrium has been established, a homogeneous, single-phase system composed of two different molecular species, uniformly and intimately mixed with each other. Such a system constitutes a " true " solution as distinguished from so-called " colloidal " solutions which are to be considered as occupying an intermediate position between true solutions, on the one hand, and heterogeneous mixtures, on the other. The subject of colloidal solutions will be discussed in a subsequent chapter.

When one substance is dissolved, or molecularly dispersed, in another, it is customary to designate as the *solvent* that component which is present in the larger proportion, and to call the other component the *solute.* It should be remembered that this method of designation is purely arbitrary, and that the ability of one substance to dissolve in another does not imply that one component possesses greater solvent power than the other. In fact, it frequently happens that two liquids are miscible in all proportions, in which case either one may be regarded as the solvent. Such liquids are said to be *consolute.*

While no general principle has as yet been discovered by means of which the solubility of one substance in another can be predicted, it is nevertheless true that solubility is to a large extent dependent upon the existence of a similarity in character between the components of a solution. For example, benzene is insoluble in water but mixes in all proportions with its homologue, toluene.

Likewise, a great number of organic compounds, such as the solid hydrocarbons and fats, which are insoluble in water, dissolve readily in ether or benzene. On the other hand, numerous inorganic salts dissolve in water over a wide range of concentration, notwithstanding the fact that they bear little or no resemblance to the solvent.

Modes of Expressing the Composition of Solutions. There are several different ways in which the composition of a solution may be expressed. A very common mode of expressing the composition of a dilute solution is in terms of *gram-molecular weight*, *formula-weight*, or *equivalent-weight* per *liter of solution*.

Thus, the concentration of a solution of sulphuric acid, ($H_2SO_4 = 2 \times 1.008 + 32.06 + 4 \times 16 = 98.08$), containing 98.08 grams per liter is said to be *molar* or *formal*, whereas the concentration of a solution which contains one equivalent, or 49.04 grams, of acid per liter is said to be *equivalent*, or *normal*. It is sometimes convenient to express the concentration of a solution in terms of 1000 grams of solvent rather than in terms of 1000 cc. of solution. A solution which contains one mol of solute in 1000 grams of solvent is termed a *molal* solution. If the solvent is water, 1000 grams of solvent will be equivalent to $1000 \div 18.016 = 55.51$ mols, and a molal solution will, therefore, contain one mol of solute in 55.51 mols of solvent. When concentrations are expressed on the basis of the weight of the solvent, they are known as *weight concentrations* to distinguish them from the *volume concentrations* previously defined. It is obvious that volume concentrations can be converted into weight concentrations, provided the densities of the solutions are known.

The composition of more concentrated solutions may be expressed, either in percentages, or in terms of *mol fractions*, preferably the latter. By the mol fraction of a dissolved substance is meant the number of mols of the substance divided by the total number of mols in the solution. Thus, if a solution is composed of n_A mols of A and n_B mols of B, the mol fractions of the two components will be as follows: —

$$x_A = \frac{n_A}{n_A + n_B} = \text{mol fraction of } A,$$

and

$$x_B = \frac{n_B}{n_A + n_B} = \text{mol fraction of } B.$$

From these two expressions it is evident that $x_A + x_B = 1$.

Classification of Solutions. There are nine possible classes of solutions, as follows: —

(1) Solution of gas in gas;
(2) Solution of liquid in gas;
(3) Solution of solid in gas;
(4) Solution of gas in liquid;
(5) Solution of liquid in liquid (liquid pairs);
(6) Solution of solid in liquid;
(7) Solution of gas in solid;
(8) Solution of liquid in solid;
(9) Solution of solid in solid.

While examples of all of these different types of solutions are known, only the more important classes will be considered here.

Solutions of Gases in Gases. In solutions of this class, the components may be present in any proportions, since gases are completely miscible. In a mixture of gases where no chemical action occurs, each gas behaves independently, the properties of the gaseous mixture being the sum of the properties of the constituents. Thus, *the total pressure of a mixture of several gases is equal to the sum of the pressures which each gas would exert were it alone present in the volume occupied by the mixture.* This law was discovered by Dalton * and is known as *Dalton's law of partial pressures.* If the partial pressures of the constituent gases be denoted by p_1, p_2, p_3, etc., and P and V represent the total pressure and the total volume of the gaseous mixture, then

$$PV = V(p_1 + p_2 + p_3 + \ldots). \qquad (1)$$

Dalton's law holds when the partial pressures are not too great, its order of validity being the same as that of the other gas laws. Dalton's law can be tested experimentally by comparing the total pressure of the gases with the sum of the pressures exerted by each gas before mixture. The possibility of measuring the partial pressure of one of the two components of a gas mixture, provided a diaphragm could be found which would be pervious to one of the gases but not to the other, was first pointed out by van't Hoff. It was shown by Ramsay,† that the walls of a vessel of palladium, when sufficiently heated, permit the free passage of hydrogen but not of nitrogen. The walls are said to

* Gilb. Ann., 12, 385 (1802).
† Phil. Mag. (5), 38, 206 (1894).

be *semi-permeable*. A sketch of the apparatus used by Ramsay in the verification of Dalton's law is shown in Fig. 63. A small vessel of palladium, P, containing nitrogen, is connected with a manometer AB, which serves to measure the pressure of the gas in P. The vessel, P, is enclosed within a larger vessel, C, which can be filled with hydrogen at known pressure. On heating P and passing a current of hydrogen at a definite pressure through C, the hydrogen enters P until the pressures due to hydrogen inside and outside are equal. The total pressure in P, measured on the manometer, is greater than the pressure in C. The difference between the two pressures is very nearly equal to the partial pressure of the nitrogen. Conversely, if a mixture of the two gases be introduced into P, which is then heated and maintained at sufficiently high temperature to insure its permeability to hydrogen, the partial pressure of the nitrogen can be determined by passing a current of hydrogen, at known pressure, through C until equilibrium is attained, as shown by the manometer. The difference between the external and internal pressures is the partial pressure of the nitrogen. This experiment has a very important bearing upon the theory of solution.

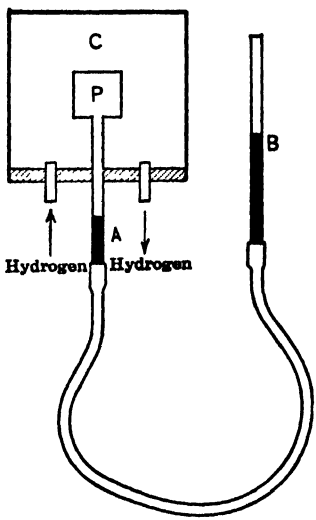

Fig. 63

Solutions of Gases in Liquids. The solubility of gases in liquids is limited, the extent to which they dissolve depending upon the pressure, the temperature, the nature of the gas, and the nature of the solvent. When a liquid cannot absorb any more of a gas at a definite temperature, it is said to be *saturated*, and the solution is called a *saturated solution*. The solubility of a gas in a liquid is defined by Ostwald as the ratio of the volume of the gas absorbed to the volume of the absorbing liquid at a specified temperature and pressure. If the solubility of the gas be represented by S, we have

$$S = v/V, \qquad (2)$$

where v is the volume of gas absorbed and V is the volume of the absorbing liquid. The "absorption coefficient" of Bunsen, in terms of which he expressed the results of his measurements of the solubility of gases, may be defined as the volume of a gas, reduced to 0° C. and 76 cm. pressure which is absorbed by unit volume of a liquid at a given temperature and under a pressure of 76 cm. of mercury. In certain cases the volume of the gas absorbed is found to be independent of the pressure, so that if α is the coefficient of gaseous expansion, and β, Bunsen's coefficient of absorption, then

$$S = \beta (1 + \alpha t). \tag{3}$$

The solubilities of a few gases in water and alcohol as determined by Bunsen are given in the following table: —

SOLUBILITY OF GASES

Gas.	Water.		Alcohol.	
	0°	15°	0°	15°
Hydrogen	0.0215	0.0190	0.0693	0.0673
Oxygen	0.0489	0.0342	0.2337	0.2232
Carbon dioxide	1.797	1.002	4.330	3.199

The solubility of gases in water is appreciably diminished by the presence of dissolved solids or liquids, especially electrolytes. Various theories have been proposed to account for the diminished solubility of gases in salt solutions, but the most satisfactory is that due to Philip,* who suggests that the phenomenon is caused by the hydration of the dissolved salt. A portion of the water in the salt solution is supposed to be in combination with the salt, the water which is thus removed from the rôle of solvent, being no longer free to absorb gas.

The solubility of a gas increases with increase in pressure. For gases which do not react chemically with the solvent, there exists a simple relation between pressure and solubility, discovered by Henry.† This relation, known as *Henry's Law* may be stated

* Trans. Faraday Soc., 3, 140 (1907).

† Gilb. Ann., 20, 147 (1805).

as follows: — *When a gas is absorbed in a liquid, the weight dissolved is proportional to the pressure of the gas.* Since pressure and volume, at constant temperature, are inversely proportional (Boyle's law), the law of Henry may be stated thus: — *The volume of a gas absorbed by a given volume of liquid is independent of the pressure.* There is yet another form in which the law may be stated which is instructive in connection with the modern theory of solution. When a definite volume of liquid is saturated with a gas at constant temperature and pressure, a condition of equilibrium is established between the gas in solution and that in the free space over the solution, therefore, Henry's law may be stated as follows: — *The concentration of the dissolved gas is directly proportional to that in the free space above the liquid.* If c_1 represents the concentration of the gas in the liquid and c_2 the concentration in the free space above the liquid, Henry's law may be expressed thus,

$$c_1/c_2 = k, \tag{4}$$

where k is known as the *solubility coefficient.*

Dalton showed that the solubility of the individual gases in a mixture of gases is directly proportional to their partial pressures, the solubility of each gas being nearly independent of the presence of the others.

As will be seen from the foregoing table, the solubility of a gas in a liquid diminishes with increase in temperature. Concerning the influence of the nature of the gas on its solubility, it may be said that those gases which exhibit acid or basic reactions are the most soluble, the solubilities of neutral gases being small. In the case of many of the very soluble gases, Henry's law does not hold. For example, ammonia, a gas having marked basic properties and a large coefficient of solubility, does not obey Henry's law at ordinary temperatures, the mass of ammonia absorbed not being proportional to the pressure. The curve showing the variation in solubility with pressure at 0° C. has two marked discontinuities. At temperatures above 100° C. the gas obeys Henry's law. Sulphur dioxide behaves similarly, the law holding only for temperatures exceeding 40° C.

With regard to the connection between the solvent power of a liquid and its nature, but little is known. About all that can be

said is, that the order of solubility of gases in different liquids is almost always the same. Thus in the preceding table the solubilities of hydrogen, oxygen and carbon dioxide in water and in alcohol will be seen to be approximately proportional. A slight change in volume always results when a gas is dissolved in a liquid. In general, it may be said that the less compressible a gas is, the greater is the increase in volume produced when it is absorbed by a liquid. It is of interest to note that the increase in volume caused by the solution of a gas is nearly equal to the corresponding value of b in the equation of van der Waals. This is shown in the following table: —

INCREASE IN VOLUME DUE TO ABSORPTION OF GAS

Gas.	Increase in Vol.	b
Oxygen	0.00115	0.000890
Nitrogen	0.00145	0.001359
Hydrogen	0.00106	0.000887
Carbon dioxide	0.00125	0.000866

Liquid Pairs.* Solutions of liquids in liquids can be divided into three classes as follows: — (1) Liquids which are miscible in all proportions; (2) Liquids which are partially miscible; and (3) Liquids which are immiscible. Examples of these three classes in the order mentioned are, alcohol and water, ether and water, and benzene and water. As to the cause of the miscibility and non-miscibility of liquids very little is known.

If a small amount of ether is added to a large volume of water in a separatory funnel and the mixture vigorously shaken, a perfectly homogeneous solution will be obtained. On gradually increasing the amount of ether, shaking after each addition, a concentration will eventually be reached at which a separation into two layers will take place. The upper layer is a saturated solution of water in ether, and the lower layer is a saturated solution of ether in water. So long as the relative amounts of the two liquids are such that the mixture does not become homogeneous

* Since immiscible liquids do not form solutions, we are hardly justified in the use of the caption, "Solutions of Liquids in Liquids" and, therefore, substitute the heading, "Liquid Pairs."

on standing, the composition of the two layers will be independent of the relative amounts of the two components. Measurements of the mutual solubility of liquids have been made by Alexejeff* by placing weighed amounts of two different liquids in sealed tubes and observing the temperature at which the mixture became homogeneous. In general the solubility of a pair of partially miscible liquids increases with the temperature, and therefore it may be inferred that at a sufficiently high temperature

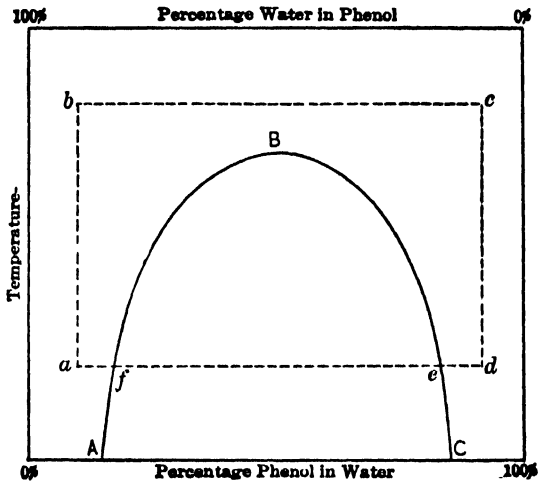

Fig. 64

the mixture will become perfectly homogeneous. An example of this type of binary mixture is furnished by phenol and water, the solubility curve of which is shown in Fig. 64. In this diagram temperature is plotted on the axis of ordinates and percentage composition of the solution on the axis of abscissæ. Starting with a small amount of phenol and adding it in increasing quantities to a large volume of water, a concentration will eventually be reached at which the solution will separate into two layers. This concentration is represented by the point A. On raising the temperature, the solubility of phenol in water increases, as shown by the curve AB. In like manner, starting with pure phenol and adding increasing amounts of water, separation into two layers will occur at a concentration repre-

* Jour. prakt. Chem., 133, 518 (1882); Bull. Soc. Chem., 38, 145 (1882).

sented by the point *C*. As the temperature is raised, the solubility of water in phenol increases, as shown by the curve *CB*. When the temperature is raised above 68°.4 C., corresponding to the point *B*, phenol and water become miscible in all proportions.

If we start with a solution whose temperature and composition is represented by the point *a*, the addition of increasing amounts of phenol, at constant temperature will be represented by the dotted line *afed*. When the point *f* is reached, the solution will separate into two layers the composition of which will be independent of the relative amounts of phenol and water. At *e* the solution will again become homogeneous. If the solution represented by the point *a* be again chosen as the starting point, and its composition be kept unaltered while the temperature is raised to a value above 68°.4 C., the change will be represented by the dotted line *ab*. If now the temperature be maintained constant and the percentage of phenol increased, the alteration in composition will be effected without discontinuity, as represented by the dotted line *bc*. On cooling the solution represented by the point *c* to the initial temperature of *a*, the point *d* will be reached. Thus it is possible to pass from *a* to *d* by the path *abcd* without causing a separation of the components into two layers. There is an analogy between the solubility curve of a pair of partially miscible liquids and the dotted, parabolic curve in the diagram of the isothermals of carbon dioxide, shown in Fig. 12. In both cases there is but one phase outside of the curves, while two phases are coexistent within the area enclosed by the curves. The analogy may be traced further, since in each case only one phase can exist above a certain temperature. The temperature corresponding to the apex of the parabolic curve in Fig. 12, is termed the critical temperature of carbon dioxide and by analogy the temperature corresponding to the point, *B*, in Fig. 64 is called the *critical solution temperature.*

The mutual solubilities of some pairs of partially miscible liquids were found by Alexejeff to diminish with increasing temperature. Thus, a mixture of ether and water, which is perfectly homogeneous at ordinary temperatures, becomes turbid on warming. A specially interesting pair of liquids is nicotine and water. At ordinary temperatures these liquids are miscible in all proportions. If the temperature is raised above 60° C., the solution becomes turbid owing to incomplete miscibility.

On continuing to heat the mixture the mutual solubility of the liquids begins to increase, until at 210° C. they become completely soluble again. The solubility relations of this binary mixture are shown in Fig. 65. The closed solubility curve defines the limits of the coexistence of two layers, all points outside of the curve representing homogeneous solutions.

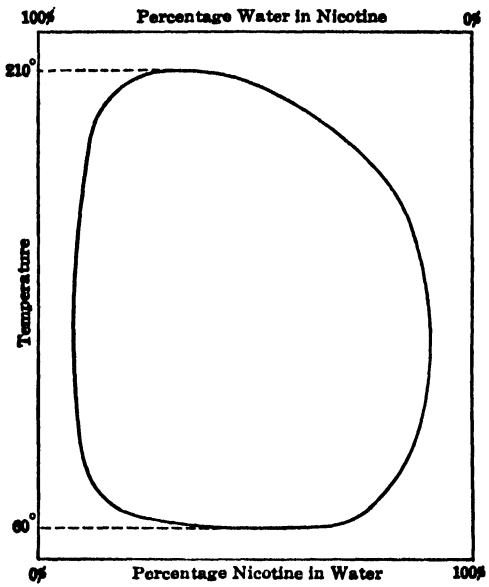

Fig. 65

Vapor Pressure of Binary Mixtures. The study of the vapor pressures of binary mixtures of completely miscible liquids is of great importance in connection with the possibility of separating them by the process of distillation. According to Henry's law, the partial pressure of a volatile solute in a solution is proportional to its concentration. Hence, it might be expected that the partial pressures of the components of a binary liquid mixture would be directly proportional to their mol fractions. It has been shown by experiment, however, that only in the case of mixtures whose components are closely related chemically, does this law obtain. Benzene and toluene afford an excellent example of a pair of liquids forming binary mixtures in which the partial pressures of the components conform very closely to the law governing ideal solutions.

The accompanying table, due to Schmidt,* gives the vapor pressures of mixtures of benzene and toluene at 20°, together with the partial pressures, calculated on the assumption that these pressures are proportional to the mol fractions of the two components. It will be seen on comparing the observed and calcu-

* Zeit. phys. Chem. 99, 80 (1921).

lated values of the total pressure, that we are justified in regarding mixtures of benzene and toluene as very close approximations to ideal solutions.

VAPOR PRESSURES OF MIXTURES OF BENZENE AND TOLUENE AT 20°

Mol Fraction Benzene	Total Press. Obs.	Partial Press. Toluene	Partial Press. Benzene	Total Press. Calc.
0.0	24.5	24.5	.....	.....
0.1	30.0	22.1	7.7	29.8
0.2	36.0	19.6	15.3	34.9
0.3	41.5	17.2	23.0	40.2
0.4	47.0	14.7	30.6	45.3
0.5	51.0	12.2	38.2	50.4
0.6	56.0	9.8	45.9	55.7
0.7	62.0	7.3	53.5	60.8
0.8	67.5	5.1	61.2	66.3
0.9	74.0	2.4	68.8	71.2
1.0	76.5	.....	76.5	76.5

In general, the lack of agreement between the observed and calculated values of the vapor pressures of binary liquid mixtures is much greater than in the case of mixtures of benzene and toluene. The following table, also due to Schmidt, gives the vapor pressures of mixtures of benzene and methyl alcohol, two liquids of widely divergent character.

VAPOR PRESSURES OF MIXTURES OF BENZENE AND METHYL ALCOHOL AT 20°

Mol Fraction Methyl Alcohol	Total Press. Obs.	Partial Press. Benzene	Partial Press. Methyl Alcohol Calc.	Total Press. Calc.
0.0	76.5	76.5	.....	76.5
0.1	106.5	68.9	9.4	78.3
0.2	128.0	61.2	18.8	80.0
0.3	139.5	53.6	28.2	81.8
0.4	144.0	45.9	37.6	83.5
0.5	145.5	38.3	47.0	85.3
0.6	145.0	30.6	56.4	87.0
0.7	145.0	23.0	65.8	88.8
0.8	141.5	15.3	75.8	91.1
0.9	123.0	7.7	84.6	92.3
1.0	94.0	.....	94.0	94.0

The preceding table serves to emphasize the fact, that the difference between actual solutions and ideal solutions becomes more apparent as the difference in character of the components becomes more pronounced. While the cause of these deviations is not known with certainty, it is believed that they may be due, either wholly or in part, to the formation of molecular complexes in the solution.

The experimental investigations of Konowalow* on homogeneous binary mixtures of liquids have shown, that they may be divided into three classes as follows:

(1) Mixtures having vapor pressures intermediate between the vapor pressures of the pure components, e.g., methyl alcohol and water; (2) mixtures having a minimum vapor pressure corresponding to a definite composition, e.g., formic acid and water; and (3) mixtures having a maximum vapor pressure corresponding to a definite composition, e.g., propyl alcohol and water.

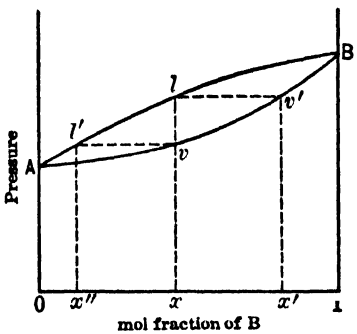

Fig. 66

In considering the possibility of separating binary liquid mixtures belonging to any one of these three classes, it is essential to determine the composition of both liquid and vapor phases. When a pure liquid is boiled the composition of the escaping vapor is the same as that of the liquid itself, but this is only true under special conditions when a binary liquid mixture is distilled.

A diagrammatic representation of the vapor pressures, at a single temperature, of all possible mixtures of two liquids *A* and *B* belonging to Class (1) are given in Fig. 66. Since the vapor pressure can be expressed in terms of the composition of either the liquid or the vapor phase, it follows that there should always be two curves in such a diagram, one referring to the liquid and the other to the vapor phase. In Fig. 66 the curves *Al'lB* and *Avv'B*, represent the variation in the vapor pressure of the liquid and vapor phases, respectively, with change in composition. The vapor phase being relatively richer in the component having the

* Wied. Ann., 14, 34 (1881).

higher vapor pressure, it follows that the curve $Avv'B$ must lie nearer to the ordinate corresponding to pure B than the curve $Bll'A$. By determining where a horizontal line cuts the two curves, we can ascertain the equilibrium concentrations of the two phases. Thus, if x denotes the mol fraction of B in the liquid phase, x' will be the equilibrium concentration of B in the vapor phase: or, if x denotes the concentration of B in the vapor phase, x'' will be the equilibrium concentration in the liquid phase.

In other words, if a binary liquid mixture whose composition is x be subjected to a process of isothermal distillation, we shall at first obtain a vapor whose composition will be x'. As the distillation proceeds, however, the composition of the liquid phase will become less rich in the component B, and assuming that none of the vapor is allowed to escape, the last drop of liquid to evaporate will have the composition represented by x'' while the corresponding composition of the vapor phase will be represented by x. Mixtures of this class can be separated into their components by fractional distillation.

Similar vapor pressure diagrams corresponding to the other two classes of binary liquid mixtures are given in Figs. 67 and 68.

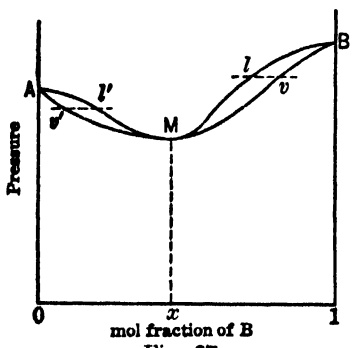

Fig. 67

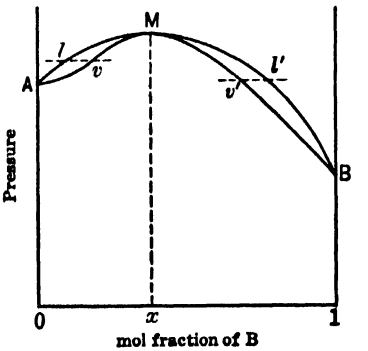

Fig. 68

Distillation of Binary Mixtures. In the preceding paragraphs we have seen that the vapor pressure curves of binary liquid mixtures at constant temperature may be divided into three classes. Similarly, when such mixtures are distilled under constant pressure, we also distinguish three corresponding classes of boiling-point curves.

In Class (1) the boiling-points of all possible mixtures are inter-

mediate between those of the two components. All mixtures belonging to Class (2) exhibit a maximum in their boiling-point curves, while the mixtures of Class (3) exhibit a minimum. Each of these three classes of curves is illustrated diagrammatically in Figs. 69 to 71. Since, in binary liquid mixtures, the lower boiling component is present in relatively greater amount in the vapor phase, it follows that in each of the three diagrams, the upper curve corresponds to the vapor phase.

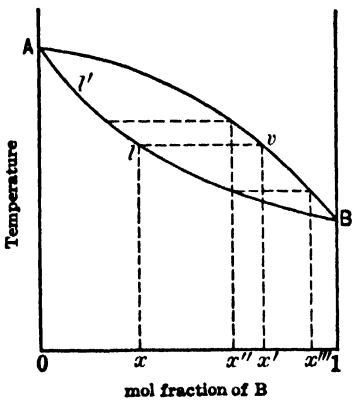

Fig. 69

Let x, Fig. 69, represent the composition of a liquid mixture belonging to Class (1). When this mixture is distilled, the first portion of vapor to condense will have the composition x' and, as distillation proceeds, the liquid phase will become gradually poorer in the component B. The vapor phase being removed by condensation, the boiling-point will continue to rise until the liquid remaining in the distilling flask is pure A.

Any binary mixture of this class can be more or less completely separated into its components by the process of *fractional distillation*. For example, if the portion of the distillate obtained while the composition of the original mixture changes from l to l' be subjected to redistillation, the average composition of the liquid in the distilling flask will be represented by x'', and the initial composition of the condensing vapor will correspond to x'''. In other words, in the process of fractional distillation, the concentration of the component B in the distillate has been increased.

Binary mixtures of Class (2) exhibit a maximum in their boiling-point curves, as shown at M in Fig. 70. On distilling a mixture whose initial composition corresponds to l, the liquid phase will become relatively richer in the component B, and the boiling-point will continue to rise until, ultimately, if the vapor be allowed to condense, the liquid phase will acquire the composition corresponding to M. This being a constant boiling mixture, it will behave in many respects like a pure compound, and will

distil without change in composition, provided the pressure remains constant. Similarly, if a mixture whose initial composition corresponds to l' be distilled, the liquid phase will become relatively richer in the component A, and finally, will acquire the composition of the mixture having the maximum boiling-point. It was thought for a long time that such constant boiling mixtures were definite chemical compounds of the two liquids. Thus, a mixture of hydrochloric acid and water containing 20.2 per cent of acid boils at 110° C. under atmospheric pressure. The composition of such a mixture corresponds very nearly to the formula, HCl. 8 H_2O. Roscoe* showed that these mixtures are not definite chemical compounds since the composition of the distillate changes when the distillation is carried out under different pressures. It is worthy of emphasis that any solution of hydrochloric acid, whatever may be its concentration, if boiled under a pressure of 760 mm. for a sufficient time, will ultimately boil at 110° and will contain 20.2 per cent HCl by weight. A partial list of binary liquid mixtures having constant maximum boiling-points under atmospheric pressure is given in the following table.

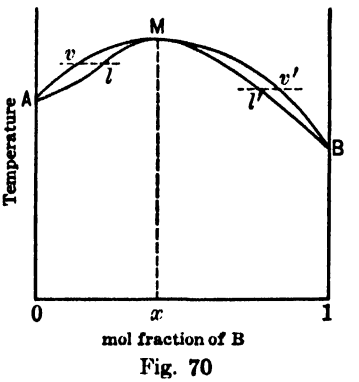

Fig. 70

BINARY MIXTURES HAVING MAXIMUM BOILING-POINTS

Components	(Pressure = 760 mm.) Boiling-Point	Composition of Mixture at B.-P.
Water + HNO_3	120.5°	68% HNO_3
Water + HCl	110	20.2% HCl
Water + HBr	126	47.5% HBr
Water + HI	127	57.0% HI
Water + HF	120	37.0% HF
Water + H.COOH	107.1	77.9% H.COOH
$CHCl_3$ + CH_3COCH_3	64.7	80.0% $CHCl_3$

A large number of pairs of liquids are also known whose boiling-point curves pass through a minimum, as shown in Fig. 71.

* Lieb. Ann., 116, 203 (1860).

These mixtures obviously belong to Class (3). Any mixture whose composition lies between that of A and M, Fig. 71, may be separated more or less completely into pure A and the mixture M by fractional distillation. In like manner, mixtures whose composition lies between that of B and M can also be separated by fractional distillation. Pure B, however, cannot be obtained on distilling a mixture whose composition lies between that of A and M. If the initial composition of a mixture belonging to this class differs but slightly from that corresponding to M, it is apparent from the diagram that the composition of the liquid phase will gradually change as the process of distillation continues. It follows, therefore, that unless great care is taken to prepare a mixture whose composition shall be exactly the same as that of M, the boiling-point will slowly rise and the composition of the mixture will undergo a gradual change. Ethyl alcohol, (b.-p. 78.3°) and water, (b.-p. 100°) furnish an interesting example of a pair of liquids belonging to this class of mixtures. The mixture containing 95.57% of alcohol by weight has a minimum boiling-point of 78.13°. Any mixture containing less than 95.57% of alcohol behaves similarly to mixtures of Class (1), and can be completely separated by fractional distillation into pure water and 95.57% ethyl alcohol. Theoretically, it should be possible to fractionate mixtures having compositions lying between 95.57% alcohol and pure alcohol; practically, however, the difference between the boiling-points of the minimum boiling mixture and that of pure alcohol is so small, that the composition of all mixtures within this range changes with extreme slowness.

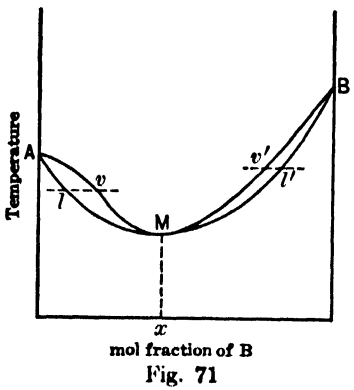

Fig. 71

We now turn to the consideration of the distillation of binary mixtures composed of partially miscible and immiscible liquids. In general when two liquids are mixed, each lowers the vapor pressure of the other, so that the vapor pressure of the mixture is less than the sum of the vapor pressures of the components. As has already been pointed out, the composition of the two layers

in a binary mixture of partially miscible liquids is independent of the relative amounts of the components present; hence the vapor pressure remains constant so long as the solution remains heterogeneous.

In general, the boiling-point curves for mixtures of two partially miscible liquids resemble those shown in Fig. 72. Mixtures in which the mol fraction of B lies between 0 and x and also between x' and 1, consist of a single homogeneous liquid phase. On the other hand, all mixtures whose composition is included between x and x' consist of two homogeneous liquid phases. If a mixture whose composition corresponds to l be distilled, the initial portions of vapor will have the composition corresponding to v. As distillation proceeds the temperature will rise and the composition of the liquid phase will alter, until eventually nothing but pure A will remain in the distilling flask. In like manner, if a homogeneous mixture whose composition corresponds to l' be distilled, the boiling-point will gradually rise, until that of the pure component B is reached. On the other hand, when any mixture whose composition lies between x and x' is distilled, the boiling-point remains constant so long as the two liquid phases are present. The composition of the two phases is represented by x and x' while the composition of the vapor from each phase is represented by x'', this being the composition corresponding to the intersection of the vapor curves, AC and BC. If the process of distillation is continued for a sufficient time, one of the two liquid phases will disappear. If the original two-phase liquid mixture was richer in component A than x'', then the phase represented by x' will disappear, and the boiling-point will increase along DA. Similarly, if the original mixture was richer in component B than x'', the phase represented by x will ultimately disappear, and the boiling-point will increase along EB. Numerous examples of mixtures of this kind are known; of these we may mention water,

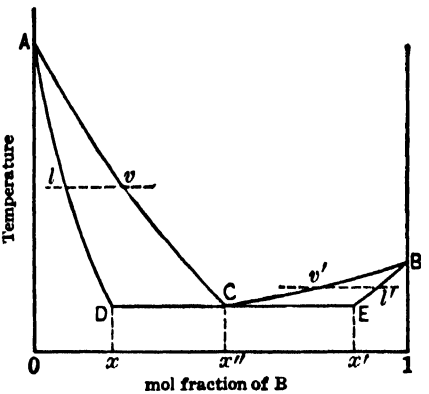

Fig. 72

(b.-p. 100°) and isobutyl alcohol, (b.-p. 108.4°) which form a two-phase mixture boiling at 88.5°, under a pressure of 760 mm.

The relation between the vapor pressure and the composition of all possible mixtures of a pair of immiscible liquids is shown diagrammatically in Fig. 73. When two such liquids are distilled from the same vessel, since neither exerts any influence upon the vapor pressure of the other, the two liquids will continue to distil in the ratio of their respective vapor pressures until one of them is completely vaporized. The straight line, *CD*, drawn parallel to the axis of composition through the ordinate corresponding to the sum of the vapor pressures of the two components, *A* and *B*, represents the relation between vapor pressure and composition. The temperature at which such a system boils will obviously be that at which the sum of the two vapor pressures is equal to that of existing atmospheric pressure. The composition of the vapor phase can be calculated in the following manner: If the vapor pressures of the two components, *A* and *B*, at the boiling point, be p_A and p_B, and if n_A and n_B be the respective number of mols of *A* and *B*, we may express the relation between vapor pressure and composition by the equation,

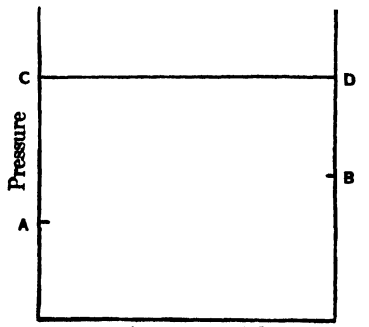

Fig. 73

$$\frac{p_A}{p_B} = \frac{n_A}{n_B}. \tag{5}$$

If w_A and w_B denote the weights in grams of *A* and *B* in a known weight of vapor (distillate), and if M_A and M_B are their respective molecular weights, we may write

$$n_A = w_A/M_A \text{ and } n_B = w_B/M_B.$$

On substituting these values in equation (5), we have

$$\frac{w_A}{w_B} = \frac{p_A}{p_B} \cdot \frac{M_A}{M_B}. \tag{6}$$

Nitrobenzene and water may be chosen as an example of a pair of liquids which are practically immiscible. Under a pressure of 760 mm. the mixture boils at 99° C. The vapor pressure of water at this temperature is 733 mm., therefore the vapor pres-

sure of nitrobenzene must be, 760 − 733 = 27 mm. Notwithstanding the relatively small vapor pressure of nitrobenzene in the mixture, considerable quantities of it distil over with the water. It is this fact that makes it possible to separate liquids by the process of *steam distillation*, so frequently employed by the organic chemist. The relative weights of water and nitrobenzene passing over in a steam distillation may be calculated as follows: — The relative volumes of steam and vapor of nitrobenzene which distil over, will be in the ratio of their respective vapor presssures at the temperature of the experiment, and consequently the relative weights of the two liquids which pass over, will be in the ratio, $p_A d_A : p_B d_B$, where p_A and p_B denote the respective vapor pressures of water and nitrobenzene, and d_A and d_B the corresponding vapor densities. If w_A and w_B denote the weights of the two liquids in the state of vapor, then

$$w_A : w_B :: p_A d_A : p_B d_B,$$

or, since vapor density is proportional to molecular weight, we may write

$$w_A : w_B :: p_A M_A : p_B M_B.$$

Substituting in this proportion the values given above for the vapor pressures of steam and nitrobenzene, we have

$$w_A : w_B :: 733 \times 18 : 27 \times 123$$

or,

$$w_A : w_B :: 13{,}194 : 3321.$$

Thus, the weights of water and nitrobenzene in the distillate are approximately in the ratio of 4 to 1, notwithstanding the fact that the ratio of their vapor pressures at the boiling-point of the mixture is 27 to 1. If an organic substance is not decomposed by steam, it is possible to effect an appreciable purification by steam distillation, even though its vapor pressure be relatively small. As will be seen from the above example, it is the high molecular weight of the nitrobenzene which compensates for its low vapor pressure. It is the small molecular weight of water which renders it so suitable for steam distillation.

Solutions of Solids in Liquids. The solubility of a solid in a liquid is limited, and is dependent upon the temperature, the

nature of the solute and the nature of the solvent. When a solvent has taken up as much of a solute as it is capable of dissolving at a definite temperature, the solution is said to be *saturated.* There are two general methods for the preparation of saturated solutions: — (1) An excess of the finely-divided solute is agitated with a known amount of the solvent, at a definite temperature, until equilibrium is attained; or (2) the solvent is heated with an excess of the solute to a temperature higher than that at which saturation is required, and then cooled in contact with the solid solute to the desired temperature. Both of these methods give equally satisfactory results, provided sufficient time is allowed for the establishment of equilibrium, and provided the solid solute is always present in excess. The solubility of solids has been shown to be somewhat dependent upon their state of division. Thus, Hulett* has found that a saturated solution of gypsum at 25° C. contains 2.080 grams of $CaSO_4$ per liter, whereas when very finely divided gypsum is shaken with this solution, it is possible to increase the content of dissolved $CaSO_4$ to 2.542 grams per liter. When a saturated solution is cooled, every trace of solid solute being excluded, the excess of dissolved solid may not separate. Such a solution is said to be *supersaturated.*

As a general rule the solubility of solids in liquids increases with the temperature, as shown in Fig. 74. Several exceptions to this rule are known, among which may be mentioned calcium hydroxide, calcium sulphate above 40° C., and sodium sulphate between the temperatures of 33° C. and 100° C.

Solubility curves are usually continuous, but exceptions to this rule are common: the solubility curve of sodium sulphate furnishes an illustration. The discontinuity in the solubility curve of sodium sulphate is due to the fact that we are not dealing with one solubility curve, but with two solubility curves. At temperatures below 33° C., the dissolved salt is in equilibrium with the decahydrate, $Na_2SO_4.10\,H_2O$, whereas at temperatures above 33° C. the dissolved salt is in equilibrium with the anhydrous salt, Na_2SO_4. The solubility of $Na_2SO_4.10\,H_2O$ increases with the temperature, while the solubility of Na_2SO_4 diminishes. That we are actually dealing with two solubility curves, is proved by the fact that the solubility curves of the hydrated and anhydrous

* Jour. Am. Chem. Soc., 27, 49 (1905).

salts in supersaturated solutions are continuations of the corresponding curves for saturated solutions, as shown by the dotted curves in Fig. 74. If we select any point, such as p, lying between a dotted curve and a full curve, it is apparent that it represents a solution supersaturated with respect to $Na_2SO_4.10\,H_2O$, but unsaturated with respect to Na_2SO_4. If pure anhydrous sodium sulphate be shaken with this solution it will slowly dissolve, whereas if a trace of the hydrated salt be added, the solution will deposit $Na_2SO_4.10\,H_2O$, until the amount remaining in solution corresponds to the solubility of the hydrate at that temperature.

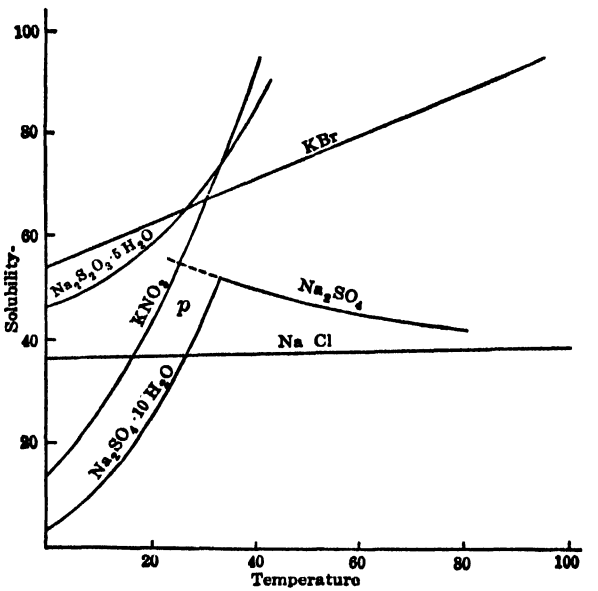

Fig. 74

Supersaturated solutions of some substances can be preserved indefinitely, provided all traces of the solid phase are excluded. Such solutions are called *metastable*. On the other hand there are some supersaturated solutions which deposit the excess of solid solute even when all traces of it are excluded. These solutions are termed *labile*. The distinction between metastable and labile solutions is not sharp. If a metastable solution is sufficiently cooled, or if its concentration is sufficiently increased, it may be made to pass over into the labile condition. The concen-

tration at which this transition occurs is termed the *metastable limit.* The stability of supersaturated solutions has been shown by Young * to be greatly influenced by vibrations or sudden shocks within the solution. He has been able to control the amount of overcooling in a supersaturated solution, by altering the intensity of the vibrations due to the friction between glass or metal surfaces within the solution.

Very little is known concerning the relation between solubility and the specific properties of solute and solvent.

Owing to the fact that the change in volume resulting from the solution of a solid in a liquid is very small, the effect of pressure on the solution is almost negligible. The chief factors conditioning the change in solubility due to increasing pressure, are the heat of solution of the solute in the nearly saturated solution, and the change in volume on solidification. Very few experiments have been made to determine the effect of pressure on solubility. It is stated by van't Hoff that the solubility of a solution of ammonium chloride, a salt which expands when dissolved, decreases by 1 per cent for 160 atmospheres, while the solubility of copper sulphate, a salt which contracts when dissolved, increases by 3.2 per cent for 60 atmospheres.

Solid Solutions. In general, when a dilute solution is sufficiently cooled, the solvent separates in the form of crystals which are almost entirely free from the solute. When, however, the temperature of a solution of iodine in benzene is reduced to the freezing-point, the crystals which separate are found to contain iodine. Furthermore, the depression of the freezing-point of the solvent is found to be less than that calculated on the assumption that the solvent crystallizes uncontaminated with the solute. Such solutions were first studied by van't Hoff.† He found that when the concentration of such abnormal solutions is varied, the ratio of the amount of solute in the liquid solvent to the amount of solute in the solidified solvent remains constant. Thus, in solutions of iodine in benzene, the ratio of the concentration of iodine in the liquid phase to its concentration in the crystallized benzene is constant. In the following table, c_1 is the concentration of iodine in the liquid benzene, and c_2 is the concentration of iodine in the solid benzene.

* Jour. Am. Chem. Soc., 33, 148 (1911).

† Zeit. phys. Chem., 5, 322 (1890).

DISTRIBUTION OF IODINE BETWEEN LIQUID AND SOLID BENZENE

a	a_1	a_1/a
3.39	1.279	0.377
2.587	0.925	0.358
0.945	0.317	0.336

It was van't Hoff who pointed out the analogy between the distribution of the solute between the solid and liquid solvent on the one hand, and the distribution of a gas between a liquid and the free space above it on the other. In other words, the distribution follows Henry's law for the solution of a gas in a liquid. Since the crystals containing both solute and solvent are perfectly homogeneous, van't Hoff suggested that they be regarded as *solid solutions.*

The mixed crystals which separate from solutions of isomorphous substances, being chemically and physically homogeneous, may also be considered as solid solutions. Many alloys possess the properties characteristic of solid solutions; hardened steel, for example, being regarded as a homogeneous solid solution of carbon in iron.

One of the characteristic properties of a dissolved substance is its tendency to diffuse into the pure solvent. Interesting experiments performed by Roberts-Austen* have shown that even solids have the property of mixing by diffusion. Thus, by keeping gold and lead in contact at constant temperature for four years, he was able to detect the presence of gold in the layer of lead at a distance of 7 mm. from the surface of separation. Many other instances of diffusion in solids have been observed.†

Instances of gases and liquids dissolving in solids are also known. Thus platinum, palladium, charcoal and other substances have the property of taking up large volumes of hydrogen. This phenomenon, known as *occlusion,* is but little understood. It was suggested by van't Hoff that when hydrogen dissolves in palladium, we are really dealing with two solid solutions, one a

* Proc. Roy. Soc., 67, 101 (1900).

† See Report on Diffusion in Solids, by C. H. Desch, Chem. News, 106, 153 (1912).

solution of hydrogen in palladium, and the other a solution of palladium in solid hydrogen, the system being analogous to that of two partially miscible liquids.

Certain natural silicates, the so-called zeolites, are transparent and homogeneous. Since they contain varying quantities of water they may be regarded as examples of solutions of liquids in solids. This classification is further justified by the fact, that portions of the water may be removed and replaced by other substances, such as alcohol, with apparently no change in the transparency or homogeneity of the mineral.

REFERENCE

Stoichiometry. Young. Chapters XII to XIV inclusive.

PROBLEMS

1. A solution of potassium chloride contains 245.7 grams of salt in 1000 grams of water, and the density of the solution at 21° is 1.1310. Calculate the weight- and volume-formal concentration of the solution. Also calculate the mol fractions of the two components of the solution.

2. A binary mixture of chloroform and acetone contains 30% of the former to 70% of the latter. Calculate the mol fractions of the components.

3. A 10% aqueous solution of sulphuric acid has a density of 1.0661 at 20°. Calculate its weight-normal and volume-molal concentrations.

4. The density of a solution of barium chloride containing 1 mol of salt to 100 mols of water is 1.0976 at 15°. What per cent of barium chloride does the solution contain? What is its volume normality with respect to barium chloride?

5. The density of a 20% aqueous solution of sodium chloride is 1.1473 at 20°. Calculate its weight-formal concentration. Express the concentrations of the two components in mol fractions.

6. 2.3 liters of hydrogen under a pressure of 78 cm. of mercury, and 5.4 liters of nitrogen at a pressure of 46 cm. were introduced into a vessel containing 3.8 liters of carbon dioxide under a pressure of 27 cm. What was the pressure of the mixture? *Ans.* 140 cm. of mercury.

7. Air is composed of 20.9 volumes of oxygen and 79.1 volumes of nitrogen. At 15° C. water absorbs 0.0299 volumes of oxygen and 0.0148 volumes of nitrogen, the pressure of each being that of the atmosphere. Calculate the composition of the mixture of gases absorbed by the water.

Ans. 34.8% by vol. of O, and 65.2% by vol. of N.

8. The vapor pressure of ethyl ether at 20° is 442.36 mm. and that of benzene is 74.66 mm. Calculate the partial pressure of each in a solution in which the mol fraction of ether is 0.4, and compute the total vapor

pressure. The observed value of the vapor pressure is 222.5 mm. What is the per cent error in the calculated pressure?

9. At 40° the vapor pressures of acetone and chloroform are 420 mm. and 366 mm. respectively. Calculate the total vapor pressure of a mixture in which the mol fraction of chloroform is 0.6. The observed value of the vapor pressure is 318 mm. Also calculate the per cent error in the calculated value of the total pressure.

10. The vapor pressures of benzene and carbon disulphide at 20°, 40°, 60° and 80° are as follows:

	20°	40°	60°	80°
C_6H_6	76.5 mm.	185 mm.	394 mm.	755 mm.
CS_2	297	617	1165	2030

Calculate the total vapor pressure at each of the above temperatures for a mixture containing one mol of benzene in one mol of carbon disulphide. The observed values of the total pressure at the above temperatures are respectively as follows: 206 mm., 432 mm., 838 mm., and 1475 mm. Calculate the per cent error for each temperature. Is the solution more nearly ideal in its behavior at the highest or lowest temperature?

11. The vapor pressure of the immiscible liquid system, aniline-water, is 760 mm. at 98° C. The vapor pressure of water at that temperature is 707 mm. What fraction of the total weight of the distillate is aniline.

Ans. 0.28

12. The boiling-point of the immiscible liquid system, naphthalene-water, is 98° C. under a pressure of 733 mm. The vapor pressure of water at 98° C. is 707 mm. Calculate the proportion of naphthalene in the distillate. *Ans.* 0.207.

CHAPTER VIII

DILUTE SOLUTIONS AND OSMOTIC PRESSURE

Osmosis. The phenomenon of osmosis, or diffusion of a liquid through a membrane, was first observed in 1748 by the Abbé Nollet, but it was not until the middle of the following century that further investigations of the phenomenon were carried out by Dutrochet and Vierordt. As a result of their studies, it was found that when a salt solution is separated from water by a suitable animal membrane, the water diffused through the membrane more rapidly than the salt. The level of the solution rose, causing an appreciable hydrostatic pressure to develop. Since this pressure was caused by the process of osmosis, it was called *osmotic pressure.*

Definition of Osmotic Pressure. The term "osmotic pressure," as defined in the preceding paragraph, lacks precision and, in view of the confusion of thought to which it has given rise, it is important that the exact meaning of the term should be made clear. The term "osmotic pressure" must not be confused with two other closely related but distinctly different quantities, known as *thermal pressure* and *diffusion pressure.* Failure to recognize these distinctions has resulted in an indiscriminate use of the term "osmotic pressure" in the literature, with a corresponding confusion of thought as to the cause of osmosis.*

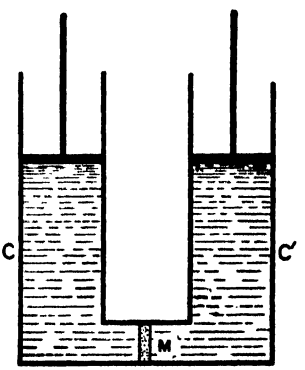

Fig. 75

The concept of osmotic pressure may readily be obtained from a consideration of the process of osmosis as interpreted by the molecular kinetic theory of liquids. In Fig. 75, let C and C' represent two cylinders each of which is filled with a pure solvent A. The cylinders are provided with tight-fitting pistons by means

* The treatment of osmotic pressure presented here is due to E. W. Washburn, "Principles of Physical Chemistry" (Second Edition), p. 190.

of which the pressure upon the contents may be increased, or diminished, as desired. A horizontal tube, connecting the cylinders, is fitted with a membrane M, which though permeable to the molecules of A is impermeable to every other species of molecule. Such a membrane is said to be "semi-permeable." Let us now assume that both cylinders and their contents are at the same temperature and under the same pressure. According to the kinetic theory, the molecules of A, being in ceaseless motion, will bombard the membrane M from both sides, and, since the concentration, temperature and pressure are the same in both C and C', it follows that as many molecules will pass through the membrane in one direction as in the other, and the pressures on the pistons will remain equal. Now let a second substance B, which is capable of forming an ideal solution with A, be dissolved in the liquid contained in C'. Since there are now fewer molecules of A per unit of volume in C', it follows that the number of molecules striking M from the right will be less than the number striking it from the left in the same interval of time. As a result of this inequality of molecular bombardment, the liquid must flow through the membrane from left to right and thus give rise to the phenomenon of osmosis. Obviously the osmotic process can be checked by changing either of the two variables, — temperature or pressure. Thus, the osmotic flow of the solvent A will be arrested if, on the one hand, the temperature of C' be raised or that of C be lowered, or on the other hand, if the pressure on C' be increased or that on C be diminished. The difference in pressure which is necessary to cause the rates of flow of the opposing streams of the molecules of A through the membrane to become equal, defines the osmotic pressure of the solution of B in A.

In the foregoing explanation of the process of osmosis it will be observed that no account has been taken of the pressure exerted on the membrane by the molecules of the solute. While it is true that the impact of the solute molecules also gives rise to a distinct pressure, it should be borne in mind that such an effect does not represent the osmotic pressure of the solution. In fact, the osmotic pressure of a solution is not to be regarded as an actual pressure exerted by a component of the solution, but rather as the difference in pressure which must be established upon the solution and solvent, respectively, in order to render the escaping tendency

of the solvent equal to that of the solution. According to this view, it follows that osmotic pressure is a definite physical quantity which is entirely independent of semi-permeable membranes or theories of osmosis.

As the pressure upon a liquid is increased, the molecules are brought nearer together, thereby causing an increase in the intensity of the molecular impacts upon the walls of the containing vessel. Hence, as the pressure upon C' is raised, the pressure on the membrane M increases, and the number of solvent molecules traversing the membrane in a unit of time also increases. It can be shown mathematically, that in a solution the osmotic pressure approaches infinity as the mol fraction of the solute approaches unity, irrespective of the natures of both solvent and solute. In other words, no finite difference in pressure, however great, would be able to check the passage of pure solvent through the semi-permeable membrane into the solution.

We have thus far considered only the case of an ideal solution in which it is not necessary to take account of the intermolecular forces which are known to be operative in all real solutions. In a concentrated solution of cane sugar, for example, the molecules of the solute undoubtedly exert a very appreciable attraction for the molecules of the solvent and, as a consequence of this attraction, the rate of osmosis suffers a corresponding change. The rate of osmosis is probably further modified by the operation of similar intermolecular forces within the semi-permeable membrane, particularly if the latter is of appreciable thickness. Obviously, the combined effect of these attractive forces will be to change the difference in pressure which must be established on the solvent and solution, respectively, in order to offset osmosis.

Diffusion Pressure. In the preceding chapter reference was made to the fact that diffusion is a characteristic property of solutions. If a few cubic centimeters of a concentrated solution of cane sugar are placed at the bottom of a tall cylinder, and water is added, care being taken to prevent mixture, the sugar immediately begins to diffuse into the water, the process continuing until the concentration of sugar is the same throughout the liquid. The sugar molecules move from a region of high concentration to a region of low concentration, the rate of diffusion being relatively slow owing to the visocity of the medium. A similar process is encountered in the study of gases, but the rate of gas-

eous diffusion is extremely rapid. In terms of the kinetic theory, the movement of the molecules of a gas from regions of high concentration to regions of low concentration, is to be considered as due to the pressure of the gas. By analogy, we may regard the process of diffusion in solutions as a manifestation of a driving force.

The molecules of the solute in the dilute solution in the cylinder C', Fig. 75, tend to diffuse into the pure solvent in the cylinder C, and as a result of the successive impacts of the solute molecules on the membrane M, a pressure is set up on the right-hand side of the membrane. The partial pressure p_D, which the solute molecules exert against a membrane which is alone permeable by the solvent molecules, is known as their *diffusion pressure*. For dilute solutions, the diffusion pressure follows the gas laws, but as the concentration is increased, it attains a definite limiting value, the magnitude and sign of which are dependent upon the temperature, the pressure and the attractive forces operative within the solution.

Thermal Pressure. According to the kinetic theory, the molecules within a solution are in ceaseless, unordered motion and their kinetic energy increases as the temperature is raised. If we assume in an ideal solution that the molecules of the solute are not subject to attraction by the molecules of the solvent, it follows that they will exert a definite pressure against a semi-permeable membrane, such as M in Fig. 75, by virtue of their kinetic energy. This pressure is known as *thermal pressure*, and may be denoted by p_T. For dilute solutions, it has been found that the thermal pressure also follows the gas laws, but as the concentration of the solution increases, the value of p_T approaches a finite limit of considerable magnitude which may be regarded as the thermal pressure of the solute molecules in the liquid state.

The relation of diffusion pressure to thermal pressure becomes apparent from a consideration of the forces acting on the molecules of the solute, B, in the immediate neighborhood of the semi-permeable membrane, M, in Fig. 75. The layer of solute molecules next to the membrane will be subjected to two opposing attractive forces: — (1) the backward pull of the molecules of both solute and solvent in the solution contained in C', and (2) the forward pull of the solvent molecules contained in C. The resultant of these opposing forces will determine the magnitude of the impact of the solute molecules on the surface of the membrane, and will thus largely determine the effective pressure which these molecules

will be able to exert. If we denote by p_A and p_B the values of the respective backward pulls of the molecules of A and B in C', and by p_A' the forward pull of the molecules of A in C, then the resultant pressure which the solute molecules will exert against the membrane will be

$$p_D = p_T + p_A' - (p_A + p_B).$$

In the case of an ideal solution,

$$p_A' = p_A + p_B,$$

for all concentrations. Hence, as the concentration of an ideal solution approaches zero, p_A' approaches p_A, and when the solution becomes infinitely dilute, $p_A' = p_A$. It follows, therefore, that in an infinitely dilute solution, the diffusion pressure of the solute molecules is equal to their thermal pressure.

The variation of the four quantities, osmotic pressure, diffusion pressure, thermal pressure and ideal gas pressure with concentration is shown graphically in Fig. 76.

The cause of the phenomenon of osmosis has repeatedly been attributed to osmotic pressure, though incorrectly and through a failure to recognize the distinctions which have just been discussed between osmotic pressure, thermal pressure and diffusion pressure, futile attempts have been made to connect the two latter with the freezing point. It should be carefully noted that while the osmotic pressure of a solution can be readily calculated from its freezing point, there is no known existing relation which connects either diffusion pressure or thermal pressure with this quantity. It is only in very dilute solutions that the values of the osmotic pressure, the thermal pressure and the diffusion pressure may be regarded as practically identical.

Semi-permeable Membranes. The use of a semi-permeable membrane for the measurement of the partial pressure of nitrogen in a mixture of nitrogen and hydrogen, has already been explained. A similar method may be employed for the measurement of the osmotic pressure of a solution, provided a suitable semi-permeable membrane can be found. While such a membrane must be impermeable to the molecules of solute it must be readily permeable to the molecules of solvent; it must exert a selective action on solute and solvent. If a solution is separated from the pure solvent by a semi-permeable membrane, diffusion of the

solute is no longer possible. Since equilibrium of the system can only be attained when the concentrations on both sides of the

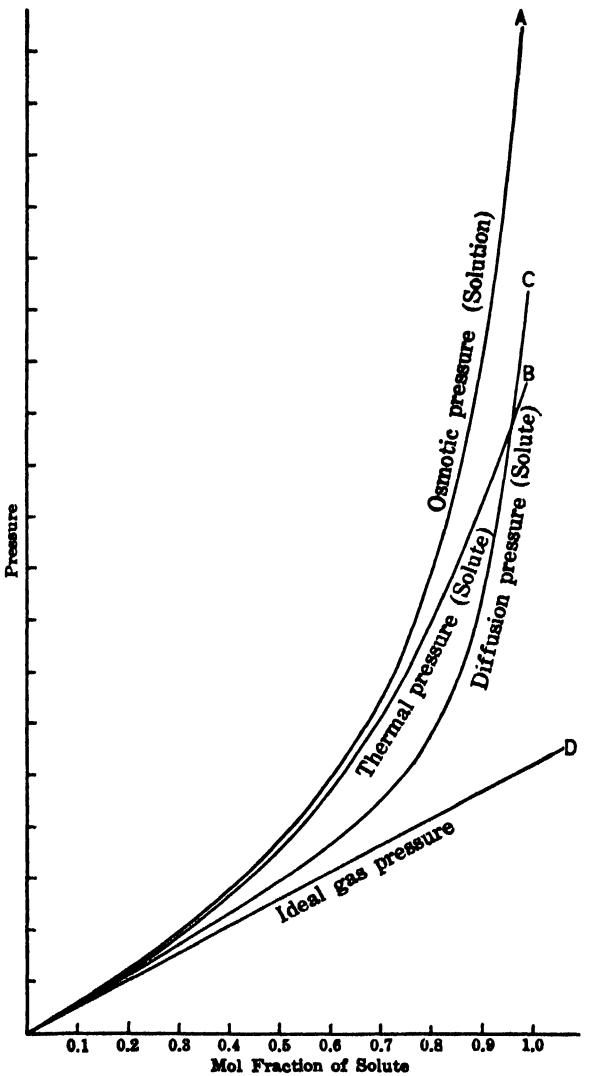

Fig. 76

membrane are equal, it follows that the solvent must pass through the membrane and dilute the more concentrated solution. A number of semi-permeable membranes have been discovered

which are readily permeable to water and nearly, if not entirely, impermeable to most solutes. About the middle of the eighteenth century Abbé Nollet discovered that certain animal membranes are permeable to water but not to alcohol.

Artificial semi-permeable membranes were first prepared by M. Traube.* If a glass tube, provided with a rubber tube and pinch-cock, be partially filled, by suction, with a solution of copper sulphate, and then immersed in a solution of potassium ferrocyanide, a thin film of copper ferrocyanide will be formed at the junction of the two solutions. When the film has once been formed, further precipitation of copper ferrocyanide will cease, the solutions on either side of the film remaining clear. Traube showed that this membrane is semi-permeable. He also showed that a number of other gelatinous precipitates possess the property of semi-permeability. A membrane formed in the above manner is easily ruptured and is wholly inadequate for quantitative or even qualitative experiments. Pfeffer† devised a method for strengthening the membrane. By depositing the precipitate in the walls of a porous clay cup, the area of unsupported membrane is greatly diminished and its resisting power correspondingly increased.

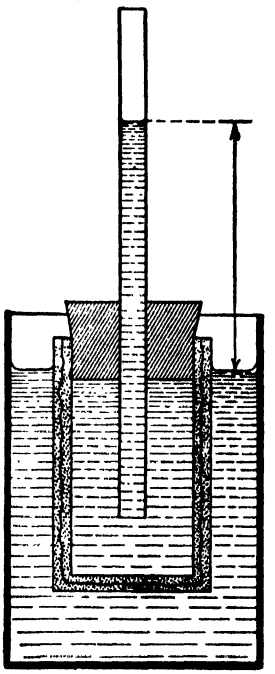

Fig. 77

Pfeffer directs that the cup to be used for this purpose must be thoroughly washed, and its walls allowed to become completely permeated with water. The cup is then filled to the top with a solution of copper sulphate, containing 2.5 grams per liter, and allowed to stand for several hours in a solution of potassium ferrocyanide, containing 2.1 grams per liter. The two solutions diffuse through the walls of the cup,

* Archiv. für Anat. und Physiol., p. 87 (1867).

† Osmotische Untersuchungen, Leipzig, 1877.

and on meeting, deposit a thin membrane of copper ferrocyanide. When precipitation is complete, the cup is thoroughly washed and soaked in water. The cup is then filled to the top with a solution of cane sugar, and a rubber stopper, fitted with a long glass tube of narrow bore, is inserted, care being taken to exclude air-bubbles. The stopper is then made fast with a suitable cement, and the cup completely immersed in a beaker of water. The completed apparatus is shown in Fig. 77. If the formation of the membrane has been successful, the level of the liquid in the vertical glass tube will slowly rise and eventually will attain a height of several meters. If the membrane is sufficiently strong and no leaks develop, the passage of water through the membrane will continue until the hydrostatic pressure of the column of liquid in the tube is great enough to overcome the tendency of the water to force its way into the sugar solution. As a general rule, the membrane becomes ruptured before equilibrium is attained.

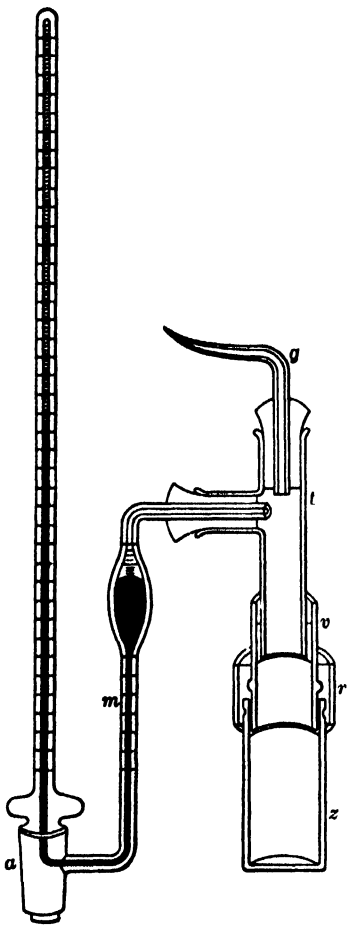

Fig. 78

Measurement of Osmotic Pressure. The first direct measurements of osmotic pressure were made by Pfeffer. His experiments deserve brief consideration, since the results obtained furnish the basis of the modern theory of solution. The cell used was similar to that described above, but instead of employing a vertical glass tube as a manometer, the cup was connected, as shown in Fig. 78, with a closed mercury manometer. The substitution of the closed for the open manometer is necessitated by the fact, that with an open manometer so much

water entered the cell that the concentration of the solution became appreciably diminished, and the pressure actually measured corresponded to a solution of smaller concentration than that introduced into the cell. With the closed manometer, when a trace of water has entered the cell, sufficient pressure is developed to prevent the further entrance of more water. Pfeffer calculated that with a cell, the capacity of which was 16 cc., the volume of water entering before equilibrium was attained, did not exceed 0.14 cc. In his experiments, Pfeffer determined the density of the cell contents before and after measurement of the osmotic pressure, and thus applied a correction for any change in concentration which might have taken place. With this apparatus he made numerous measurements of the osmotic pressures of different solutions, the entire apparatus being immersed in a constant-temperature bath.

With solutions of cane sugar he obtained the results given in the accompanying table, where C denotes the percentage concentration of the solution, and P the corresponding osmotic pressure, expressed in centimeters of mercury. The temperature varied from 13.5° C. to 14.7° C.

RELATION OF OSMOTIC PRESSURE TO CONCENTRATION

C	P	P/C
1	53.5	53.5
2	101.6	50.8
4	208.2	52.0
6	307.5	51.2

It is evident from these results, that the osmotic pressure is proportional to the concentration of the solution, since P/C is approximately constant. The deviations from constancy in the ratio of pressure to concentration may be ascribed to experimental errors, since the difficulties involved in these measurements are very great. Pfeffer also studied the influence of temperature on osmotic pressure, and showed that as the temperature is raised the pressure increases. The following table gives his results for a 1 per cent solution of cane sugar.

RELATION OF OSMOTIC PRESSURE TO TEMPERATURE

Temperature.	Osmotic Pressure.
	cm.
6°.8	50.5
13°.2	52.1
14°.2	53.1
22°.0	54.8
36°.0	56.7

Osmotic Pressure and the Nature of the Membrane. Pfeffer investigated the effect of the nature of the membrane on osmotic pressure. In addition to copper ferrocyanide, he used membranes of calcium phosphate and Prussian blue. His results seemed to indicate that the magnitude of the osmotic pressure developed, was dependent upon the nature of the membrane used.

The variations observed have since been shown, however, to have been due to leakage of the calcium phosphate and Prussian blue membranes, the copper ferrocyanide membrane being the only one which was capable of withstanding the pressure. Ostwald * has demonstrated theoretically that osmotic pressure must be independent of the nature of the membrane employed in measuring it. Thus, let A and B, in Fig. 79, represent two different semi-permeable membranes placed in a glass tube of wide bore. Let us imagine the space between the two membranes to be filled with a solution, and the tube immersed in a vessel of water. If the osmotic pressures developed at A and B are p_1 and p_2 respectively, and p_2 is less than p_1, then water will pass through A until the pressure p_1 is reached. Since the pressure at B only reaches the value p_2, however, the pressure p_1 can never be attained, and a steady stream of water from A to B, under the pressure $p_1 - p_2$, will result. This, however, would be a perpetual motion, and since this is impossible, the osmotic pressures at the two membranes must be the same.

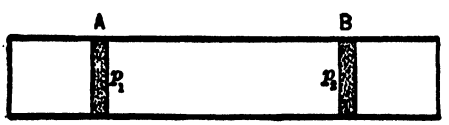

Fig. 79

Theoretical Value of Osmotic Pressure. The physico-chemical significance of Pfeffer's results was first perceived by van't

* Lehrb. d. allg. Chem., I., p. 662.

Hoff.* In a remarkably brilliant paper, he pointed out the existence of a striking parallelism between the properties of gases and the properties of dissolved substances.

We have already called attention to the analogy between osmotic pressure and gas pressure: we now proceed to trace the connection between osmotic pressure, volume and temperature, as first pointed out by van't Hoff. Pfeffer's experiments showed that at constant temperature, the ratio, P/C, is constant for any one solute. Since the concentration varies inversely as the volume in which a definite amount of solute is dissolved, we obtain, by substituting $1/V$ for C, the equation, PV = constant, which is plainly the analogue of the familiar equation of Boyle for gases. An examination of Pfeffer's data for osmotic pressures at different temperatures, convinced van't Hoff that the law of Gay-Lussac is also applicable to solutions. In the following table, the osmotic pressures in atmospheres for a 1 per cent solution of cane sugar at different temperatures are recorded, together with the pressures calculated on the assumption that the osmotic pressure is directly proportional to the absolute temperature.

VARIATION OF OSMOTIC PRESSURE WITH TEMPERATURE

Temperature.	P (obs.).	P (calc.).
6°.8	0.664	0 665
13°.7	0.691	0.681
15°.5	0.684	0.686
22°.0	0.721	0.701
32°.0	0.716	0 725
36°.0	0.746	0.735

Since the laws of Boyle and Gay-Lussac are both applicable, we may write an equation for dilute solutions corresponding to that already derived for gases, or

$$PV = R'T, \qquad (1)$$

in which P is the osmotic pressure of a solution containing a definite weight of solute in the volume, V, of solution, T being the absolute temperature of the solution and R' a constant corresponding to the molecular gas constant.

The molecular gas constant R has already been evaluated and

* Zeit. phys. Chem., 1, 481 (1887).

has been found to be equal to 0.0821 liter-atmosphere. Making use of Pfeffer's data, van't Hoff calculated the value of R' in the above equation, in the following manner: the osmotic pressure of a 1 per cent solution of cane sugar at 0° C. is 0.649 atmosphere, and since the concentration of the solution is 1 per cent, the volume of solution containing 1 mol of sugar, will be 34,200 cc. or 34.2 liters. Substituting these values in the equation, we have

$$R' = \frac{PV}{T} = \frac{0.649 \times 34.2}{273} = 0.0813 \text{ liter-atmos.},$$

a value which is nearly the same as that of the molecular gas constant, R. The equality of R and R' leads to a conclusion of the greatest importance, as was pointed out by van't Hoff, viz., "*the osmotic pressure exerted by any substance in solution is the same as it would exert if present as a gas in the same volume as that occupied by the solution, provided that the solution is so dilute that the volume occupied by the solute is negligible in comparison with that occupied by the solvent.*" It should be remembered that we are not justified in concluding from this proposition that osmotic pressure and gaseous pressure have a common origin. While the origin of osmotic pressure may be kinetic, it is also conceivable that it may result from the mutual attraction of solvent and solute, or that it may bear some relation to the surface tension of the solution. Up to the present time no wholly satisfactory explanation of the cause of osmotic pressure has been advanced.

Just as 1 mol of gas at 0° C. and 760 mm. pressure occupies a volume of 22.4 liters, so when 1 mol of a substance is dissolved, and the solution diluted to 22.4 liters at 0° C., it will exert an osmotic pressure of 1 atmosphere. In other words, *molar weights, or quantities proportional to molar weights, of different substances, when dissolved in equal volumes of the same solvent exert the same osmotic pressure.* If we deal with n mols of solute instead of 1 mol the general equation becomes,

$$PV = nRT. \tag{2}$$

But $n = g/M$, where g is the number of grams of solute and M is its molecular weight. Substituting in the preceding equation, we have

$$PV = g/M \cdot RT,$$

or,

$$M = \frac{gRT}{PV}. \qquad (3)$$

Since P, V, g, R and T are all known, M can be calculated. The direct measurement of the osmotic pressure of a solution does not afford a practical method for the determination of the molecular weight of a dissolved substance, because of the experimental difficulties involved and the time required for the establishment of equilibrium. There are other and simpler methods for determining molecular weights in solution, based upon certain properties of solutions which are proportional to their respective osmotic pressures.

The Direct Measurement of Osmotic Pressure. It is only within the past twenty years that the investigations of Pfeffer have been confirmed and extended by the elaborate and systematic experiments of Morse and his co-workers,* on the direct measurement of osmotic pressure. The most important of the improvements introduced by Morse are the following: — (1) the improvement of the quality of the membrane; (2) the improvement of the connection between the cell and the manometer, and (3) the improvement of the means of accurately measuring the pressure. The membrane of copper ferrocyanide was deposited electrolytically. After thorough washing and soaking in water, the porous cup, made from specially prepared clay, was filled with a solution of potassium ferrocyanide and immersed in a solution of copper sulphate. An electric current was then passed from a copper electrode in the solution of copper sulphate, to a platinum electrode immersed in the solution of potassium ferrocyanide. This drove the copper and ferrocyanide ions toward each other, and the membrane of copper ferrocyanide was thus formed in the walls of the cup. The passage of the current was continued until the electrical resistance reached a value of about 100,000 ohms. The cell was rinsed, and soaked in water for several hours, and then the electrolytic treatment was repeated until the electrical resistance attained a maximum value. A solution of cane sugar was now introduced into the cell, which, after connecting with the manometer, was immersed in water. When the pressure had attained its maximum value, the apparatus was dismantled and the cell, after thorough washing and soaking in water,

* Carnegie Inst. Publ. 198, (1914).

was again subjected to the electrolytic process of membrane formation. In this manner the weak places in the membrane were repaired, and by continued repetition of the treatment, a membrane possessing maximum resistance was ultimately obtained.

The following table, taken from the papers of Morse and his students, shows that when concentrations are expressed on the weight-molar basis, there is direct proportionality between osmotic pressure and concentration over a comparatively wide range of both concentration and temperature.

OSMOTIC PRESSURES OF SUCROSE SOLUTIONS IN ATMOSPHERES

Conc.	0°		20°		40°		60°		Av. Ratio
	Press.	Ratio	Press.	Ratio	Press.	Ratio	Press.	Ratio	
0.1	2.462	1.106	2.590	1.130	2.560	0.998	2.717	1.000	1.06
0.2	4.723	1.065	5.064	1.060	5.163	1.012	5.438	1.001	1.03
0.4	9.443	1.060	10.137	1.060	10.599	1.037	10.866	1.000	1.04
0.6	14.381	1.077	15.388	1.071	16.146	1.053	16.535	1.015	1.05
0.8	19.476	1.091	20.905	1.093	21.806	1.068	22.327	1.025	1.07
1.0	24.826	1.130	26.638	1.130	27.701	1.085	28.367	1.045	1.10

In the columns headed " Ratio ", are given the ratios of the measured values of osmotic pressure to the corresponding calculated values of gas pressure.

The investigations of Morse and his co-workers may be summarized thus: — (1) the law of Boyle is applicable to dilute solutions, provided the concentration is referred to 1000 grams of solvent and not to 1 liter of solution; (2) the law of Gay-Lussac is also applicable to dilute solutions, that is, the temperature coefficients of osmotic pressure and gas pressure are equal, and (3) the small departures from the theoretical values of the osmotic pressures may be traced to hydration of the solute.

Direct measurements of the osmotic pressure of concentrated solutions of cane sugar, dextrose and mannite have also been made by the Earl of Berkeley and E. G. J. Hartley.* The method employed by these investigators differs from that of Pfeffer or Morse, in that the tendency of water to pass through the semi-permeable membrane is offset by the application of a counter

* Proc. Roy. Soc., 73, 436 (1904); Trans. Roy. Soc. A., 206, 481 (1906).

pressure to the solution. The apparatus of Berkeley and Hartley is shown diagrammatically in Fig. 80. A membrane of copper ferrocyanide is deposited electrolytically very near the outer surface of a tube of porous porcelain. This tube is placed co-axially within a large cylindrical vessel of gun metal, an absolutely tight joint between the two being secured by an ingenious system of der-

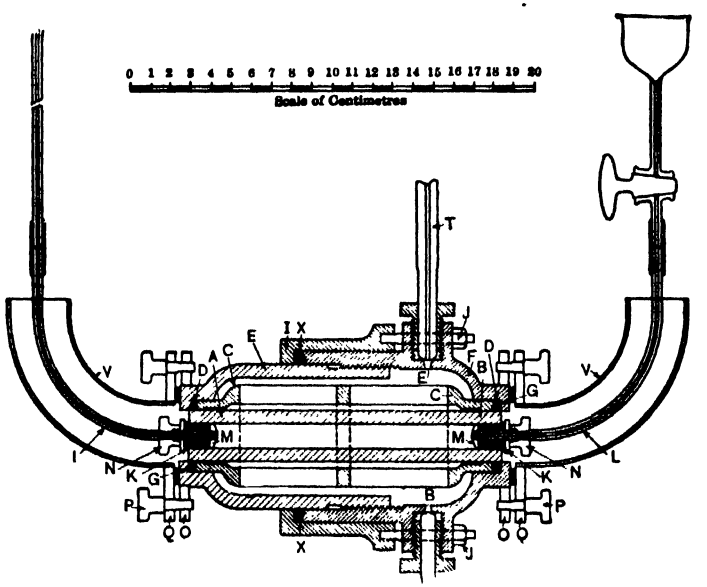

Fig. 80

matine rings and clamps. The open ends of the porcelain tube are closed by rubber stoppers fitted with capillary tubes bent at right angles, one of the latter being provided with a glass stop-cock. When a determination of osmotic pressure is to be made, the apparatus is placed in a horizontal position and water is introduced into the porcelain tube, completely filling it and the connecting capillary tubes up to a certain level. The gun metal vessel is then filled with the solution, and connected with an auxiliary apparatus by means of which a gradually increasing hydrostatic pressure can be applied. If no pressure is applied to the solution, water will pass through the semi-permeable membrane into the solution, and

the level of the water in the capillary tubes will fall. In carrying out a measurement, therefore, as soon as the solution is introduced into the gun metal vessel, hydrostatic pressure is applied, the magnitude of the pressure being so adjusted as to counterbalance the osmotic pressure of the solution. The level of the water in the capillary tubes serves to indicate the relative magnitudes of the osmotic and hydrostatic pressures. When the level of the water in the capillary tubes remains constant, the two pressures are in equilibrium. The following table gives the values of the equilibrium pressures of solutions of cane sugar, at 0° C. It must be remembered that when the two pressures are in equilibrium, there is always a pressure of one atmosphere on the solvent.

OSMOTIC PRESSURE OF SUCROSE SOLUTIONS IN ATMOSPHERES

(Temperature 0°)

Conc. gm. per Liter.	Press. (Obs.)	Press. (Calc.)
180.1	13.95	13.95
300.2	26.77	28.74
420.3	43.97	32.55
540.4	67.51	41.85
660.5	100.78	51.16
750.6	133.74	58.14

As will be seen, the pressures developed in the more concentrated solutions are enormous, and it is a surprising fact, that even in cases where the highest pressures were measured, hardly a trace of sugar was found in the pure solvent, proving that over the entire range of pressures the membrane retained its property of semi-permeability. The figures in the third column are calculated on the assumption that there is direct proportionality between osmotic pressure and concentration. It is apparent that in every case the observed osmotic pressure is greater than the calculated. Even when the concentrations are expressed on the weight-molal basis, as recommended by Morse, the osmotic pressure increases more rapidly than the concentration.

This is well shown in the accompanying diagram, Fig. 81, due

to the Earl of Berkeley. In this diagram, the osmotic pressures of solutions of cane sugar are plotted against concentrations. Curve A represents the actually observed osmotic pressures; curve C is traced on the assumption that osmotic pressure may be calculated from the equation, $PV = RT$, where V denotes the volume of solvent containing 1 mol of cane sugar; and curve B,

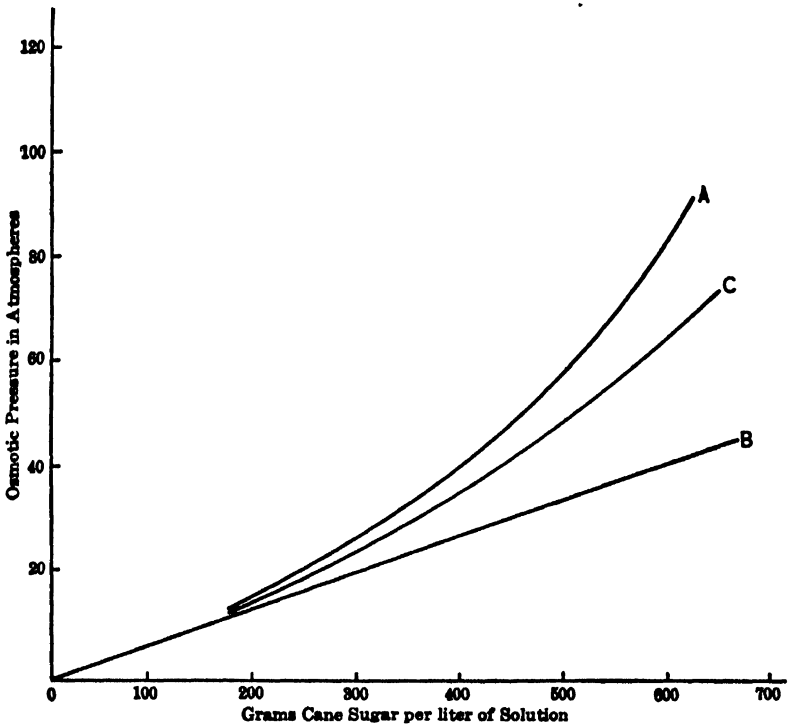

Fig. 81

a straight line, is drawn on the assumption that osmotic pressure may be calculated from the equation, $PV = RT$, where V represents the volume of solution containing 1 mol.

While the theoretical and observed values of the osmotic pressure are approximately equal in the more dilute solutions, it is obvious that the observed values of the osmotic pressure of the concentrated solutions are always greater than the calculated

values, even when the calculation is made on the assumption that V, in the equation $PV = RT$, is the volume of the solvent. The abnormally high osmotic pressures observed by the Earl of Berkeley have been discussed by Callendar* who suggests hydration of the solute as a probable cause. He shows, that if 5 molecules of water are assumed to be associated with each molecule of cane sugar in the most concentrated solutions studied by the Earl of Berkeley, the discrepancy between the observed and calculated values of the osmotic pressure disappears.

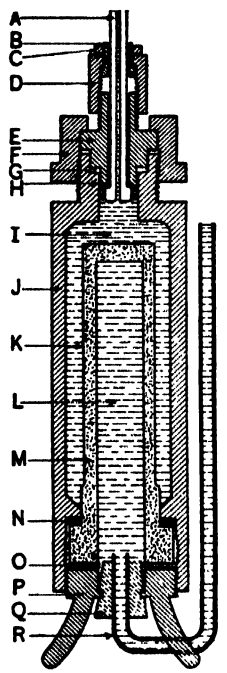

Fig. 82

Frazer and Myrick† have recently devised an ingenious modification of the method originated by Morse. By means of this new apparatus equilibrium can be established within a few hours, and osmotic pressures of at least 270 atmospheres can be measured. These features make it possible to determine the osmotic pressures of concentrated solutions with a high degree of accuracy and also suggest the possibility of determining the osmotic pressures of electrolytes. In this new form of apparatus, a diagram of which is shown in Fig. 82, the membrane is deposited on, and in the pores near, the outer surface of the cell. The cell is fastened inside of a hollow bronze cylinder to which the manometer is attached. The solution to be studied is placed inside the cylinder and around the clay cell, the solvent being placed inside the latter. It will be seen that the position of the membrane is similar to that in the apparatus of Berkeley and Hartley.

However, instead of applying mechanical pressure to the solution until equilibrium was established, as in the apparatus of Berkeley and Hartley, the solution was allowed to develop its own pressure, as in the apparatus of Morse. The mercury manometer of the Morse apparatus was replaced by an electrical resistance gauge in which use is made of the principle that the electrical

* Proc. Roy. Soc. A., 80, 466 (1908).

† Jour. Am. Chem. Soc. 38, 1907 (1916).

resistance of certain metallic conductors increases very nearly linearly with the pressure. By means of this gauge it was possible to measure pressures far in excess of those which the mercury manometer can withstand. The following table gives the results of measurements of the osmotic pressures of sucrose solutions covering the complete range of solubility.

OSMOTIC PRESSURE OF SUCROSE SOLUTIONS IN ATMOSPHERES

(Temperature 30°)

Conc. gm. per 1000 gm. H_2O	Press. (F. & M.)	Press. (B. & H.)
202	15.59	15.48
370	29.78	29.72
569	47.88	48.81
820	73.06	74.94
1133	109.10	111.87
1430	148.80	148.46

The values given in the last column are calculated from the data of Berkeley and Hartley for sucrose solutions at 0°, as given in the preceding table, p. 228.

Frazer and Lotz* have further improved the apparatus of Frazer and Myrick by substituting the water interferometer, as a manometer, in place of the electrical resistance gauge, the zero of which was found to undergo a gradual shift due to hysteresis effects in the resistance coils. The possibility of employing the water interferometer as a pressure gauge, is based upon the fact that when pressure is applied to a solution in one of the chambers of the interferometer, the index of refraction of the solution is increased, and the magnitude of the applied pressure can be measured by the resultant displacement of the interference fringes. With this apparatus, osmotic pressures up to 273 atmospheres have been measured, while the time required for the establishment of equilibrium has been very appreciably reduced.

Lowering of Vapor Pressure. It has long been known that the vapor pressure of a solution is less than that of the pure sol-

* Jour. Am. Chem. Soc. 43, 2501 (1921).

vent, provided the solute is non-volatile. The investigations of von Babo and Wüllner* on the lowering of vapor pressure of various liquids when non-volatile substances are dissolved in them, resulted in the following generalizations: — (1) *The lowering of the vapor pressure of a solution is proportional to the amount of solute present;* and (2) *For the same solution, the lowering of the vapor pressure of the solvent by a non-volatile solute is at all temperatures a constant fraction of the vapor pressure of the pure solvent.*

In 1887, Raoult,† as the result of an exhaustive experimental investigation, enunciated the following laws: — (1) *When equimolecular quantities of different non-volatile solutes are dissolved in equal volumes of the same solvent, the vapor pressure of the solvent is lowered by a constant amount;* and (2) *The ratio of the observed lowering of the vapor pressure to the vapor pressure of the pure solvent is equal to the ratio of the number of mols of solute to the total number of mols in the solution.* The ratio of the observed lowering to the original vapor pressure is called the *relative lowering of the vapor pressure.* Letting p_0 and p denote the vapor pressures of solvent and solution, Raoult's second law may be formulated thus,

$$\frac{p_0 - p}{p_0} = \frac{n}{N + n} = x, \tag{4}$$

in which n and N represent the number of mols of solute and solvent respectively, and x is the mol fraction of the solute.

On rearranging, equation (4) becomes

$$p = p_0 \frac{N}{N + n} = p_0 x_0, \tag{5}$$

where x_0 is the mol fraction of the solvent. Some of Raoult's results for ethereal solutions are given in the accompanying table. The figures in the last column of the table, headed K, give the lowering of the vapor pressure produced by dissolving one mol of solute in 100 grams of solvent. The mean value of $\frac{p_0 - p}{np_0}$ for 14 different solutes studied by Raoult was 0.0098; this is in very

* Pogg. Ann., 103, 529 (1858).

† Compt. rend., 104, 1430 (1887); Zeit. phys. Chem., 2, 372 (1888); Ann. Chem. Phys. (6), 15, 375 (1888).

LOWERING OF THE VAPOR PRESSURE OF ETHER PRODUCED BY VARIOUS SOLUTES

Solutes.	Mol. Wt.	n	$\frac{p_0 - p}{p_0}$	$\frac{p_0 - p}{np_0}$	K
Methyl salicylate.....	152	2.91	0.026	0.0089	0.71
Methyl benzoate.....	136	9.60	0.091	0.0095	0.70
Benzoic acid.....	122	7.175	0.070	0.0097	0.71
Trichloracetic acid.....	163.5	11.41	0.120	0.0105	0.71
Caprylic alcohol.....	130	6.27	0.069	0.0110	0.73
Aniline.....	93	7.66	0.081	0.0106	0.71

close agreement with the theoretical value of the relative lowering of a 1 molar per cent solution calculated as follows: —

$$\frac{p_0 - p}{p_0} = \frac{1}{100 + 1} = 0.0099.$$

When the solution is very dilute, the number of mols of solute is negligible in comparison with the number of mols of solvent, and the equation of Raoult may be written in the form,

$$\frac{p_0 - p}{p_0} = \frac{n}{N}. \tag{6}$$

Since $n = g/m$, and $N = W/M$, where g and W are the weights of solute and solvent respectively, and m and M are the corresponding molecular weights, the above equation becomes

$$\frac{p_0 - p}{p_0} = \frac{gM}{Wm}. \tag{7}$$

This equation enables us to calculate the molecular weight of a dissolved substance from the relative lowering of the vapor pressure produced by the solution of a known weight of solute in a known weight of solvent. Solving the equation for m, we have

$$m = \frac{gM}{W} \cdot \frac{p_0}{p_0 - p}. \tag{8}$$

As an illustration of the application of this equation, we may take the determination of the molecular weight of ethyl benzoate from the following experimental data: — The vapor pressure at

80° C. of a solution of 2.47 grams of ethyl benzoate in 100 grams of benzene is 742.6 mm.: the vapor pressure of pure benzene at 80° C. is 751.86 mm. Substituting in the equation, we have

$$m = \frac{2.47 \times 78}{100} \cdot \frac{751.86}{751.86 - 742.6} = 156.$$

The molecular weight calculated from the formula, $C_6H_5COO.C_2H_5$, is 150.

Vapor Pressure of a Dilute Solution and Henry's Law. It is worthy of note that Raoult's law is in reality merely a special case of Henry's law. According to the latter, the amount of gas which dissolves in a given volume of a solvent is proportional to the partial pressure of the gas above the solution. (See p. 192.) If the concentration of the gas be expressed in terms of the mol fraction, Henry's law may be represented by the equation,

$$p = kx, \tag{9}$$

where x is the mol fraction of the solute and k is a constant characteristic of the solute in a given solvent. On comparing equation (9) with equation (5) they will be seen to differ only in their proportionality factors.

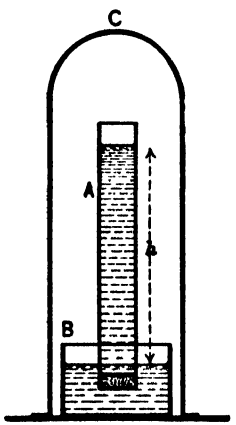

Fig. 83

Connection between Lowering of Vapor Pressure and Osmotic Pressure. The relation between osmotic pressure and the lowering of vapor pressure has been derived in the following manner by Arrhenius.* Imagine a very dilute solution contained in the wide glass tube A, Fig. 83. The tube, A, is closed at its lower end with a semipermeable membrane, and dips into a vessel, B, which contains the pure solvent. The entire apparatus is covered by a bell-jar C, and the enclosed space exhausted. Let h be the difference in level between the solvent and solution when equilibrium is established, that is, when the hydrostatic pressure of the column of liquid is equal to the osmotic pressure. When equilibrium is attained, the vapor pressure of the solution at the height h

* Zeit. phys. Chem., 3, 115 (1889).

will be equal to the pressure of the vapor of the solvent at this height. If the vapor pressure of the pure solvent in the vessel, B, is p_0, and if p is the vapor pressure of the solution at the height, h, we shall have

$$p_0 - p = hd, \tag{10}$$

where d denotes the density of the vapor. Let v be the volume of 1 mol of solvent in the state of vapor, then

$$p_0 v = RT,$$

and

$$v = \frac{RT}{p_0}.$$

If the molecular weight of the solvent is M, we may replace v by M/d, when the preceding equation becomes

$$\frac{M}{d} = \frac{RT}{p_0},$$

or,

$$d = \frac{Mp_0}{RT}. \tag{11}$$

The solution being very dilute, the osmotic pressure may be calculated from the equation

$$PV = nRT,$$

where P is the osmotic pressure of the solution, V the volume of the solution and n the number of mols of solute present. If s represents the density of the solvent, and also of the solution, (the latter being very dilute), we may write

$$P = hs,$$

and

$$V = \frac{g}{s},$$

where g is the number of grams of the solvent in which the n mols of solute are dissolved. Substituting these values of P and V in the general equation, we have

$$PV = nRT = hg,$$

and solving for h, we have

$$h = \frac{nRT}{g}. \tag{12}$$

Substituting the values of d and h, given in equations (11) and (12), in equation (10), we have

$$p_0 - p = \frac{nRT}{g} \cdot \frac{Mp_0}{RT} = \frac{nMp_0}{g}. \tag{13}$$

Rearranging equation (13), and remembering that $N = g/M$, we obtain

$$\frac{p_0 - p}{p_0} = \frac{n}{N}. \tag{14}$$

This equation, it will be seen, is identical with that derived experimentally by Raoult for very dilute solutions.

By an application of thermodynamics to dilute solutions, van't Hoff showed that the relation between osmotic pressure and the relative lowering of the vapor pressure may be expressed by the equation

$$\frac{p_0 - p}{p_0} = \frac{MP}{sRT},$$

in which the symbols have the same significance as above. This equation may be reconciled easily with the equation of Raoult.

Thus, if n in equation (14) be replaced by its equal, PV/RT, the equation becomes

$$\frac{p_0 - p}{p_0} = \frac{PV}{NRT}. \tag{15}$$

But $V = NM/s$, hence,

$$\frac{p_0 - p}{p_0} = \frac{MP}{sRT}. \tag{16}$$

This equation shows that the relative lowering of the vapor pressure is directly proportional to the osmotic pressure.

While the laws of Raoult and van't Hoff are thus seen to be identical for extremely dilute solutions, it should be pointed out that they yield widely differing results when applied to concen-

trated solutions. It has been found that the experimental data obtained with a large number of solutions over an extended range of concentration are in far closer agreement with the law of Raoult than with the law of van't Hoff. While the equation expressing the law of van't Hoff may, by the introduction of empirical constants, be so modified as to yield results which are in fairly close agreement with established experimental data, yet, in general, the law of Raoult is to be regarded as the more dependable.

Fugacity. In the preceding treatment of ideal solutions, the assumption has been made that the vapor of a liquid behaves as a perfect gas and that the tendency of the molecules to escape is measured by their vapor pressure. Although this assumption is permissible in the case of ideal solutions it cannot be made in the case of actual solutions. This difficulty has been successfully surmounted by Lewis* through the introduction of a quantity which accurately represents the escaping tendency, and which he terms the *fugacity*. According to Lewis, — " The fugacity bears to the vapor pressure a relation analogous to the relation between the perfect gas thermometer and a thermometer of some actual gas. The fugacity will be equal to the vapor pressure when the vapor is a perfect gas, and in general, it may be regarded as an " ideal " or " corrected " vapor pressure.

The relation of the fugacity, f, to vapor pressure is defined mathematically by the equation

$$\left(\frac{\partial \ln f}{\partial p}\right) = \frac{v}{RT}. \tag{17}$$

Several methods have been devised by Lewis for the evaluation of the fugacity, but only one will be outlined here. If the deviation of a vapor from the gas laws be denoted by A, we may write

$$v = \frac{RT}{p} - A. \tag{18}$$

On substituting in equation (17), we have

$$\left(\frac{\partial \ln f}{\partial p}\right) = \frac{1}{p} - \frac{A}{RT},$$

* Lewis, Zeit. phys. Chem., 38, 205 (1901).

which becomes, on integrating,

$$RT \ln f = RT \ln p - \int_0^p A dp. \tag{19}$$

By plotting A against p, and determining the area under the curve between the indicated limits, the numerical value of the fugacity may be determined. As the pressure decreases, the value of A has been found to approach a constant limiting value and, therefore, it follows from equation (19), that

$$ln \frac{f}{p} = -\frac{Ap}{RT},$$

or

$$\frac{f}{p} = 1 - \frac{Ap}{RT} = \frac{pv}{RT}. \tag{20}$$

Since the pressure, P, of a perfect gas is equal to RT/v, it follows that

$$\frac{f}{p} = \frac{p}{P}. \tag{21}$$

As an illustration of the foregoing equations we will calculate the fugacity of fluorbenzene. The saturation pressure of C_6H_5F is 1.974 atmospheres at $T = 382.0°$, and its molal volume under these conditions is 15,000 cc. Assuming the vapor to follow the gas laws, the pressure of this volume of vapor would be $RT/v = 82.07 \times 382 \div 15{,}000 = 2.085$ atmospheres. Substituting this for P in equation (21), we have

$$\frac{f}{1.974} = \frac{1.974}{2.085},$$

or

$$f = 1.87 \text{ atmospheres}.$$

In other words, the fugacity differs from the vapor pressure by 0.104 atmosphere, or very nearly 6 per cent.

Activity. It frequently happens that it is either impossible or exceedingly difficult to determine the numerical value of the fugacity of one of the components of a solution at each of two concentrations. It is a comparatively simple matter, however, to determine the ratio of the fugacities, and therefore, it has proven

advantageous to employ the ratio between the fugacity f, of a substance in any given state, to its fugacity f_0, in an arbitrarily chosen standard state, at a given temperature. This relative fugacity, known as the *activity*, may be defined by the equation

$$\frac{f}{f_0} = \alpha. \tag{22}$$

It follows, therefore, that we may write equation (5), summarizing Raoult's law, in the form

$$f = f_0 x_0, \quad \text{or} \quad \alpha = x_0. \tag{23}$$

In like manner, the change in free energy, ΔF, accompanying the transference of one mol of one of the components of a solution from the pure liquid state to an infinite amount of solution, may be shown to be expressed by the equation

$$F = RT \ln f/f_0 = RT \ln \alpha, \tag{24}$$

or

$$F = RT \ln x_0. \tag{25}$$

The Measurement of Vapor Pressure. The difficulties which attend the accurate measurement of the vapor pressure of a solution by the static method have already been mentioned. While there are other methods which are preferable for the determination of the molecular weight of dissolved substances, the vapor pressure method has one marked advantage — it can be used for the same solution at widely divergent temperatures. The method devised by Walker, and already described in connection with the determination of the vapor pressure of pure liquids (p. 76), is well adapted to the measurement of the vapor pressure of solutions.

The fundamental importance of accurate determinations of the lowering of the vapor pressure of various solvents by dissolved substances has long been recognized. With this end in view, the inherent defects in both the static and dynamic methods have been made the subject of numerous investigations, and during the past decade improved forms of apparatus have been developed which have raised these methods to the rank of methods of precision.

The outstanding difficulties in all static methods are: (1) the complete removal, from the solution, of dissolved gases and other constituents more volatile than the solvent; and (2) the prevention of inequalities in concentration throughout the solution. These

difficulties have been almost completely overcome by Frazer and Lovelace,* who have devised a form of apparatus in which provision is made for the removal of dissolved air, and for complete renewal of the entire surface of the solution by vigorous stirring. In this apparatus, use is made of the principle of the Rayleigh manometer† to measure the difference between the

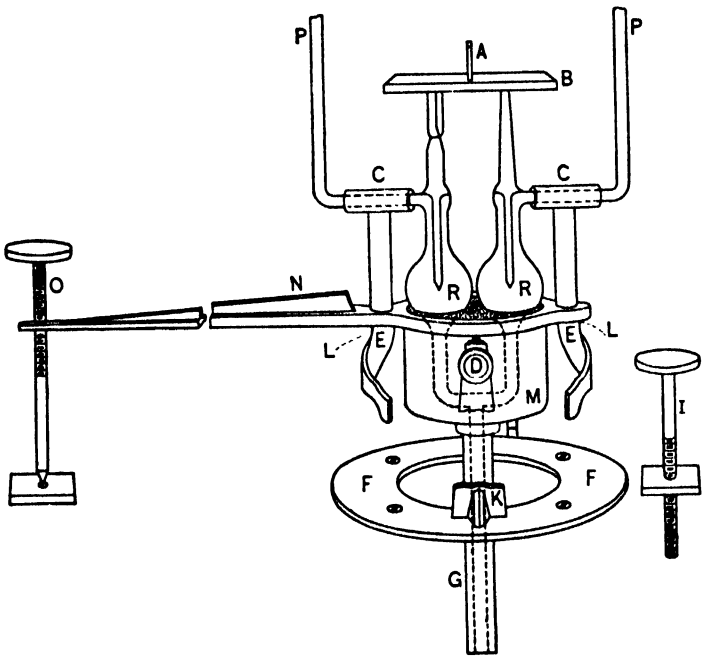

Fig. 84

vapor pressure of the solution and that of the pure solvent. The essential features of this extremely sensitive pressure gauge are shown in Fig. 84. The following description is taken from the original paper of Frazer and Lovelace. "The two glass bulbs *RR*, about 39 mm. in diameter, are blown on a glass fork. This is connected by means of a rubber tube with a mercury reservoir, which may be adjusted very accurately at any desired height by means of the screw *I*. At the centers of the bulbs are set two glass points. The side limbs, *PP*, communicate with the systems,

* Jour. Am. Chem. Soc., 36, 2439 (1914).
† Trans. Roy. Soc., 196, 205 (1901).

the relative pressures in which are to be measured. The bulbs are set in plaster in an iron pot, M, which is mounted on an axis, D, at right angles to the vertical plane passing through the points. This permits of rotation by means of the screw O.

Now, suppose the same pressure exists in the two bulbs. By manipulation of the two screws I and O, the one serving to regulate the height of the mercury and the other to rotate the manometer, the two points can readily be brought into coincidence with their images in the mercury. This is called the zero position.

Now, suppose the pressure in one bulb to be slightly increased. By readjustment of the mercury level and again rotating, the points can a second time be brought into coincidence with their images. It is obvious that, in order to calculate the difference in pressure in the two bulbs, it is necessary to know very accurately the distance between the points and the angle of rotation. The angle of rotation may be calculated from the length of the lever arm, and the rotation and pitch of the screw O. Or, following Rayleigh, we may determine the difference in pressure by means of a mirror, telescope and scale, and this is the method actually used. A is a metallic mirror firmly mounted in a vertical plane perpendicular to the line joining the two glass points. The axis of rotation lies in the plane of the mirror. A telescope, with vertical scale, is mounted at a distance of a little over three meters in front of the mirror, the image of the scale being at all times visible through the telescope.

If d represents the distance between the points, D the distance from mirror to scale, θ the angle of rotation from the zero position, h the difference in pressure in the two limbs of the manometer corresponding to this angle of rotation, and S the scale deflection, then the following equations are obtained:

$$h = d \sin \theta \quad \text{and} \quad S = D \tan 2\theta;$$

and

$$h = \frac{dS}{2D} \frac{\sin \theta}{\frac{1}{2} \tan 2\theta}.$$

Now for all values of θ up to 1°, $\frac{\sin \theta}{\frac{1}{2} \tan 2\theta}$ may be regarded as unity and our formula becomes, $h = dS/2D$. For the particular instrument being used in this work $\theta = 1°$ corresponds approximately to the depression of a 3-molar solution of a non-electrolyte,

$d = 38.88$ mm. and $D = 3350.6$ mm. Substituting these values and making $S = 1$ we get $h = \frac{38.88 \times 1}{2 \times 3350.6} = 0.00580$. This means that 1 mm. scale deflection from zero position corresponds to a difference in pressure in the two bulbs of 0.00580 mm. By observing the points through microscopes of 25 mm. focus, mounted on the instrument and rotating with it, the operator can set the points to an accuracy of 0.1 mm on the scale, which corresponds to a difference in pressure of 0.00058 mm. This is the limit of accuracy of the instrument, and is approximately that claimed by Rayleigh for his manometer, of which the one used in this work is practically a reproduction."

In using an instrument of such precision the authors are subjecting the static method of measuring vapor pressures to the severest test that could be applied. The results, however, have fully justified its use.

In the following table are given the results of a series of measurements of the lowering of the vapor pressure of water produced by mannite.

VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF MANNITE *
(Temperature 20°)

Conc. Wt. Molal	Vapor pressure lowering		Lowering per mol solute (Obs.)
	(Obs.)	(Calc.)	
0.0984	0.0307	0.0311	0.3113
0.1977	0.0614	0.0622	0.3108
0.2962	0.0922	0.0931	0.3133
0.3945	0.1227	0.1239	0.3107
0.4938	0.1536	0.1547	0.3111
0.5944	0.1860	0.1858	0.3129
0.6934	0.2162	0.2164	0.3118
0.7927	0.2478	0.2469	0.3126
0.8922	0.2792	0.2775	0.3129
0.9908	0.3096	0.3076	0.3124

* Frazer, Lovelace and Rogers, Jour. Am. Chem. Soc., 42, 1793 (1920).

In the dynamic, or air-saturation method, of determining vapor pressures, the chief sources of error are, (1) in the measurement of the volume of aspirated air, and (2) in maintaining a constant temperature during the successive determinations of the vapor

pressures of the solvent and the solution. These difficulties may be overcome by so arranging the apparatus that the same quantity of air is passed over the solution and solvent in succession, both liquids being contained in similar "saturators" which are immersed in a thermostat. The losses in weight of solution and solvent, due to the removal of the vapor of the latter, may be determined either by weighing the saturators before and after an experiment, or by absorbing the moisture which is present in the saturated air in suitable weighed absorption apparatus. The former method has been followed by Berkeley, Hartley, and Burton,* while Washburn and Heuse† have adopted the latter. Both methods give excellent results. The following table contains the results of Berkeley, Hartley, and Burton for solutions of sucrose at 0°.

VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF SUCROSE
(Temperature 0°)

Concentration Gms. Solute to 100 Gms. Solvent	$\frac{l_0}{l_1}$	Osmotic Press. in atmos. (Calc.)	Osmotic Press. in atmos. (Obs.)
56.50	1.03612	43.91	43.84
81.20	1.05566	67.43	67.68
112.00	1.08340	100.53	100.43
141.00	1.11342	134.86	134.71
183.00	1.15908	186.86	.....
217.50	1.19963	230.70	.....
243.00	1.23060	264.46	.....

The second column of the table gives the ratio of the sum of the observed losses of weight of the solution and water saturators, l_0, to the corresponding loss in the solution saturators, l_1. The third column gives the values of the osmotic pressure as calculated from the corresponding vapor pressure lowerings, while the last column contains the observed values of the osmotic pressure as determined by Berkeley and Hartley.‡

Elevation of the Boiling-Point. Just as the vapor pressure of a solution is less than that of the pure solvent, so the boiling-point of a solution is correspondingly higher than the boiling-point

* Phil. Trans. Roy. Soc., A. 209, 177 (1909); 565, 295 (1919).
† Jour. Am. Chem. Soc., 37, 309 (1915).
‡ loc. cit.

of the solvent. It follows that when equimolecular quantities of different substances are dissolved in equal weights of the same solvent, the elevation of the boiling-point is constant. Thus, the molecular weight of any soluble substance may be determined by comparing its effect on the boiling-point of a particular solvent, with that of a solute of known molecular weight. The elevation in boiling-point produced by dissolving 1 mol of a solute in 1000 grams of a solvent is termed the *molar elevation*, or *boiling-point constant* of the solvent. In determining the boiling-point constant of a solvent, a fairly dilute solution is employed and the elevation in the boiling-point is observed; the value of the constant is then calculated on the assumption that the elevation in boiling-point is proportional to the concentration.

If g grams of a substance of unknown molecular weight m, are dissolved in G grams of solvent, and the boiling-point is raised dT_b degrees, then, since m grams of the substance when dissolved in 1000 grams of solvent, produce an elevation of K_b degrees (the molar elevation), it follows that

$$\frac{1000\,g}{G} : dT_b :: m : K_b,$$

therefore,

$$m = 1000\,K_b \frac{g}{G\,dT_b}. \tag{26}$$

The accompanying table gives the molar boiling-point constants for some of the more common solvents.

MOLAR BOILING-POINT CONSTANTS *

Solvent	Boiling-Point at 760 mm.	dp/dT atmos./degree	K_b	Correction per 10 mm.
Acetic acid	118.51	0.0308	3.28	0.08
Benzene	80.51	0.0309	2.58	0.24
Carbon disulphide	46.00	0.0325	2.40	0.20
Chloroform	60.19	0.0329	3.64	0.10
Ethyl alcohol	78.26	0.0379	1.24	0.10
Ethyl ether	34.42	0.0358	2.21	0.07
Ethyl acetate	77.13	0.0317	2.90	0.12
Methyl alcohol	64.67	0.0399	0.84	0.09
Methyl formate	31.92	0.0377	1.63	0.10
Methyl acetate	57.11	0.0345	2.20	0.09
Propyl alcohol	97.14	0.0365	1.71	0.12
Water	100.00	0.0358	0.518	0.07

* Rosanoff and Dunphy, Jour. Am. Chem. Soc., 36, 1414, (1914).

The figures given in the last column are to be used in correcting the molar boiling-point constant for changes in barometric pressure: the corrections are to be added to K_b for every 10 mm. increase in pressure over 760 mm., and subtracted for every 10 mm. decrease below 760 mm.

Osmotic Pressure and Boiling-Point Elevation. Imagine a dilute solution containing n mols of solute in G grams of solvent, and let dT_b be the elevation in the boiling-point. Suppose a large quantity of the solution to be introduced into a cylinder, fitted with a frictionless piston, and closed at the bottom by a semi-permeable membrane. Let the cylinder and contents be raised to the absolute temperature T, the boiling-point of the solvent, and then let pressure be exerted on the piston just sufficient to overcome the osmotic pressure of the solution. In this way, let a quantity of solvent corresponding to 1 mol of solute be forced through the semi-permeable membrane. The volume V, thus expelled is the volume corresponding to G/n grams of solvent. If the osmotic pressure of the solution is P, then the work done in moving the piston and expelling the solvent is PV. Now let the portion of the solvent which has been forced through the semi-permeable membrane be vaporized. For this operation, $G/n.L_v$ calories will be required, L_v being the heat of vaporization for 1 gram of solvent at its boiling-point. Then let the entire system be raised to the boiling-point of the solution, $(T + dT_b)$, the previously expelled G/n grams of vapor being allowed to mix with the solution. The heat of vaporization lost at T, is thus recovered at the slightly higher temperature, $(T + dT_b)$. Finally, the entire system is cooled to T, and is thus restored to its original state.

But for a reversible cyclical process, we have

$$dW = Q\frac{dT_b}{T}, \text{ (see equation (37) p. 176)}$$

and hence, by substitution, we obtain the expression

$$\frac{PV}{\frac{G}{n}\cdot L_v} = \frac{dT_b}{T},$$

therefore,

$$dT_b = \frac{PVT}{L_v}\cdot\frac{n}{G}. \qquad (27)$$

But, since $PV = RT$, equation (16) may be written,

$$dT_b = \frac{RT^2}{L_v} \cdot \frac{n}{G}.$$

If $n = 1$ and $G = 1000$ grams, then $dT_b = K_b$ (the molar elevation of the boiling-point), or

$$K_b = \frac{RT^2}{1000\, L_v}.$$

Or putting $R = 2$ calories, we have

$$K_b = \frac{0.002\, T^2}{L_v}. \tag{28}$$

Equation (27) shows that *the osmotic pressure of a solution is directly proportional to the elevation of the boiling-point.*

Equation (28) was originally derived by van't Hoff at about the time when Raoult determined the values of K_b experimentally. The calculated values of K_b are in close agreement with the values obtained experimentally by Raoult and others. As an example, the calculated value of the molecular elevation for water, the heat of vaporization of which at 100° C. is 537 calories, is

$$K_b = \frac{0.002 \times (373)^2}{537} = 0.518,$$

a value which is in exact agreement with that given in the table.

Experimental Determination of Boiling-Points. One of the simplest and most convenient of the various forms of apparatus which have been devised for the determination of the boiling-points of solutions, is that developed by Mathews * from an earlier form of apparatus described by Bigelow. † In this apparatus, the heat is supplied electrically, this having been found to be far superior to gas heating in which protecting mantles, glass beads and various other troublesome accessories are necessary. A diagram of the apparatus is shown in Fig. 85. It will be seen to consist of a boiling vessel A, closed by a cork stopper, through which pass a Beckmann thermometer, the return tube from the condenser and the two small glass tubes B containing the wires through which the current is led to the platinum heating coil. The boiling vessel

* Trans. Am. Electrochem. Soc. 19, 81 (1911).

† Am. Chem. Jour., 22, 280 (1899).

is entirely enveloped within an un-silvered Dewar cylinder *C*. Circulation of air between the boiling vessel and the vacuum jacket is prevented by means of a rubber gasket, or by cotton packing. The bulb of the thermometer is placed in the center of the large vertical coil, as shown in the diagram. Bubbles of vapor in rising do not touch the bulb of the thermometer, but rise directly to the surface of the liquid. The vortex motion produced by the ascending stream of bubbles serves to stir the liquid very effectively. The flattened bottom of the boiling vessel makes it possible to bring the heating coil so close to the lower end of the vessel that inequality of temperature, due to a more or less stagnant layer of liquid, is avoided. The heating elements consist of two strands of platinum wire 0.38 mm. in diameter and about 20 cm. in length. These are twisted together and a current of from 10 to 14 amperes is used. With a current of this strength there is far less superheating than when a coil of finer wire and greater length is used with a current of lower amperage. The constancy of the current is controlled by means of a suitable rheostat with a sliding contact. Inasmuch as constancy of boiling-point is largely dependent upon the constancy of the rate at which the condensed and cooled liquid returns from the condenser, it is very necessary that heat be supplied at a perfectly fixed rate. Naturally such accurate control is all the more necessary when large currents are sent through small resistances, but this is a requirement easily satisfied, and constitutes no objection to the use of the heavier currents. The condensed liquid drops freely from the condenser to the violently agitated boiling liquid below. Fluctuations in temperature always result if the liquid runs down the thermometer, the outside walls or the

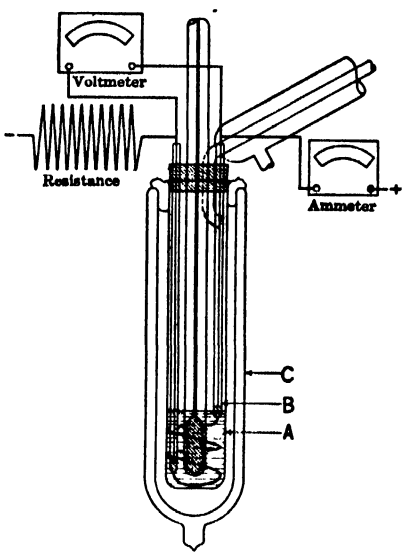

Fig. 85

glass tubes, these fluctuations being due to imperfect mixing. A known weight of liquid in *A* is boiled until the thermometer remains constant; this temperature is taken as the boiling-point of the liquid. The apparatus is now emptied and dried. A weighed amount of solute is added and the boiling-point of the solution is determined. By means of a capillary siphon a sample of the solution may be removed for analysis. The difference between the readings of the thermometer when immersed in the solution, and in the solvent alone, gives the boiling-point elevation.

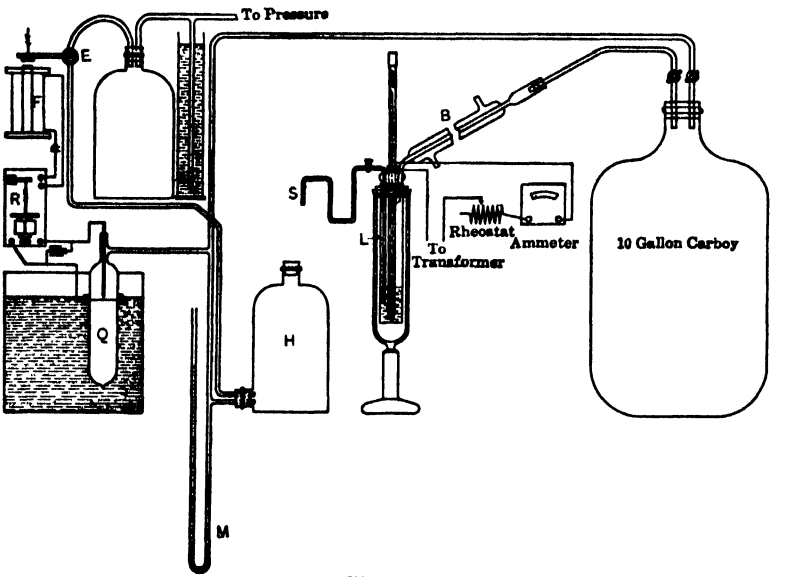

Fig. 86

The accuracy of the results obtainable with the foregoing apparatus may be greatly enhanced by connecting it with a manostat, in order that constant pressure may be maintained within the boiling vessel throughout an experiment. Such a method of pressure control has recently been developed by Mathews* and is here briefly described.

The bulb *Q*, Fig. 86, is immersed in a thermostat, constant to $\pm 0.02°$. It is made in two parts, each cemented into a heavy, flat brass ring; these are bolted together with a thin spring-steel diaphragm between, and the joints made tight by rubber gaskets.

* Carroll, Rollefson and Mathews, Jour. Am. Chem. Soc., 47, 1791 (1925).

The lower portion contains air at constant temperature and, therefore, constant pressure. The upper portion is connected by a side tube to the rest of the apparatus. A small piece of platinum foil is soldered to the upper side of the diaphragm; a threaded brass rod, working through a nut sealed into the upper part of the bulb, carries a sharp platinum wire which can be brought into contact with the foil.

Assume a fall of pressure in the apparatus. The diaphragm bulges, making contact with the wire. This actuates the relay R, energizing the electromagnet, F, and opening the valve E, which admits air under pressure into the system until the contact again opens. A condenser is connected across the contact to reduce sparking. The opening through the valve E is small, and the volume of the system is increased by introducing the carboy and the bottle, H, to reduce the rate of change in pressure. The connecting tubing should be at least 8 mm. in diameter. With the apparatus described, the diaphragm being 5 cm. in diameter and about 0.1 mm. thick, the change in pressure on operation is barely visible on the water manometer, M, which indicates difference in pressure between the apparatus and the atmosphere, that is, less than 0.02 mm. of mercury. The temperature of the boiling liquid in L can be maintained constant to 0.001° for over an hour at a time. It is advisable to have sufficient leakage (best deliberately introduced by a capillary outlet) so that the valve operates several times a minute. The necessity of the pressure regulator is evident when one considers that the boiling point of most solvents is changed 0.001° by 0.03 to 0.04 mm. change in pressure.

In determining the boiling-point of a pure liquid, it is customary to place the bulb of the thermometer in the vapor of the boiling liquid. Under these conditions, the thermometer bulb becomes coated with a thin film of the liquid in contact with its vapor, and, by thus avoiding superheating, an extremely accurate determination of the boiling-point of the liquid is insured. In determining the boiling-point of a solution, however, where the thermometer bulb is immersed in the liquid, there is always an appreciable error due to superheating, and at best, the observed boiling-point is to be regarded as only an approximation to the true boiling-point of the solution.

An ingenious form of boiling-point apparatus has been devised

* Jour. Am. Chem. Soc., 41, 721 (1919).

by Cottrell* by means of which it is possible to secure a perfect equilibrium between the liquid and vapor phases of a solution, and to determine with a high degree of accuracy the temperature of this equilibrium. The novel feature of this form of boiling-point apparatus consists in placing the thermometer bulb in the vapor phase, as in the case of a pure liquid, and causing the boiling liquid to pump some of itself over the thermometer bulb in a thin film, thus reproducing, as far as possible, the same relations of vapor and liquid to the thermometer as exist in determinations of the boiling-point of a pure liquid.

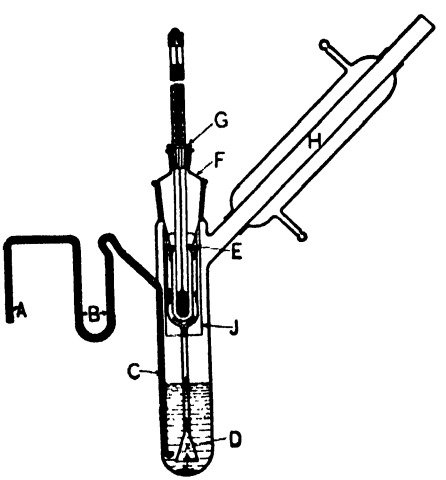

Fig. 87

The apparatus is shown diagrammatically in Fig. 87. The tube *D* functions as a pump, and insures the passage of an intimate mixture of solution and vapor over the thermometer bulb. A glass sheath, *J*, is attached to the ground glass stopper and serves to protect the thermometer bulb from the cooling influence of the condensed solvent as it flows back into the boiling vessel. The solute is introduced through the condenser tube *H*. When the boiling-point of a solution becomes constant to within 0.001°, the source of heat is momentarily removed and the capillary U-tube, *B*, is surrounded by a bath of ice water. By applying air pressure at the open end of the condenser tube, *H*, a sample of the solution can be removed for analysis. In this way the exact concentration of the liquid phase can be obtained.

The following table contains the results of an investigation, on the boiling-points of solutions of naphthalene in benzene carried out with the Cottrell apparatus by Washburn and Read.*

The figures in the first column give the values of the measured elevations of the boiling-point, while those of the second column give the corresponding concentrations expressed as mol fractions

* Jour. Am. Chem. Soc., 41, 721 (1919).

of solute. The values of the concentrations, calculated on the assumption that the solutions obey Raoult's law are given in the last column.

BOILING-POINTS OF SOLUTIONS OF NAPHTHALENE IN BENZENE

dT_b(obs.)	z_1 (obs.)	z_1 (calc.)
1.478	0.04169	0.04293
2.430	0.07012	0.06938
3.890	0.10779	0.10820
4.967	0.13529	0.13553
5.238	0.14220	0.14236
6.368	0.17204	0.16947

Lowering of the Freezing-Point. Of all the methods employed for the determination of molecular weights in solution, the freezing-point method is the most accurate and the most widely used. It was pointed out by Blagden* over a century ago, that *the depression of the freezing-point of a solvent by a dissolved substance is directly proportional to the concentration of the solution.* When equimolecular quantities of different substances are dissolved in equal volumes of the same solvent, the lowering of the freezing-point is constant. The molecular weight of any soluble substance can be found, as in the boiling-point method, by comparing its effect on the freezing-point of a solvent with that of a solute of known molecular weight. *The molar lowering of the freezing-point, or the freezing-point constant, of a solvent is defined as the depression of the freezing-point produced by dissolving* 1 *mol of solute in* 1000 *grams.* The freezing-point constants of a few common solvents are given in the following table.

A formula analogous to that employed for the calculation of the molecular weight of a dissolved substance from the elevation it produces in the boiling-point of a solvent, may be used for the calculation of molecular weight from freezing-point depression. Thus, if g grams of solute, when dissolved in G grams of solvent, produce a depression dT_f in the freezing-point of the solvent, the molecular weight m, is given by the formula,

$$m = 1000\, K_f \cdot \frac{g}{G \cdot dT_f}, \tag{29}$$

where K_f is the molecular lowering of the freezing-point.

* Phil. Trans., 78, 277 (1788).

MOLAR FREEZING-POINT CONSTANTS

Solvent	Freezing-Point	Molar Depression, K_f.
Acetic acid	17	3.9
Benzene	5.4	5.12
Benzil	94	10.5
Bromine	−7.3	9.7
Ethylene bromide	10	12.5
Formic acid	8	2.8
Naphthalene	80	6.8
Nitrobenzene	5.3	7.0
Phenol	38.5	7.4
Tribromphenol	95	20.4
Urethane	49	5.14
Water	0	1.855
p-Xylol	16	4.3

Osmotic Pressure and Freezing-Point Depression. Let dT_f be the freezing-point depression produced by n mols of solute in G grams of solvent, the solution being dilute. Imagine a large quantity of this solution to be confined within a cylinder fitted with a frictionless piston, and the bottom of the cylinder to be closed by a semi-permeable membrane. Let the cylinder and contents be cooled to the freezing temperature of the solvent T, and then let pressure be applied to the piston until a quantity of solvent corresponding to 1 mol of solute is forced through the semi-permeable membrane. This requires an expenditure of energy equivalent to PV, where P is the osmotic pressure of the solution and V is the volume of solvent expelled. The volume V is clearly the volume of G/n grams of solvent. Now let the expelled portion of solvent be frozen, and the system thereby deprived of $\frac{G}{n} L_f$ calories of heat, where L_f is the heat of fusion of 1 gram of the solvent at the temperature T. The temperature of the solution is then lowered to its freezing-point $(T - dT_f)$, and the G/n grams of solidified solvent dropped into it. The solidified solvent melts, thereby restoring to the system at the temperature $(T - dT_f)$, the heat of fusion formerly taken from it. Finally, the temperature of the system is raised to T, the initial temperature of the cycle. Applying the familiar thermodynamic relation,

$$dW = Q\frac{dT_f}{T} \text{ (see equation (37) p. 176),}$$

we have

$$\frac{PV}{\frac{G}{n}L_f} = \frac{dT_f}{T}. \tag{30}$$

From which we obtain

$$dT_f = \frac{PVT}{L_f} \cdot \frac{n}{G}.$$

But $PV = RT$, hence equation (30) becomes

$$dT_f = \frac{RT^2}{L_f} \cdot \frac{n}{G}.$$

If $n = 1$ and $G = 1000$ grams, then $dT_f = K_f$, the molar lowering of the freezing-point, and

$$K_f = \frac{RT^2}{1000\,L_f}.$$

Or putting $R = 2$ calories, we have

$$K_f = \frac{0.002\,T^2}{L_f}. \tag{31}$$

It is evident from equation (30) that *the osmotic pressure of a solution is directly proportional to the freezing-point depression.*

The agreement between the observed and the calculated values of K_f is very satisfactory, as the following calculation for water shows: —

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86.$$

It is of interest to note that the calculated value of K_f for water is lower than the experimental values originally obtained by Raoult and others. Subsequent experiments, carried out with greater care and better apparatus, by Raoult, Abegg and Loomis gave values in close agreement with that derived theoretically.

Experimental Determination of Freezing-Points. The apparatus almost universally employed for the determination of molecular weights by the freezing-point method is that devised by Beckmann,* and shown in Fig. 88. It consists of a thick-walled test tube A, provided with a side tube, and fitted into a wider tube A_1. The whole is fitted into the metal cover of a large

* Zeit. phys. Chem., 2, 683 (1888).

battery jar, which is filled with a freezing mixture whose temperature is several degrees below the freezing-point of the solvent. The tube A is closed by a cork stopper, through which pass the thermometer and stirrer. The thermometer is generally of the Beckmann differential type.

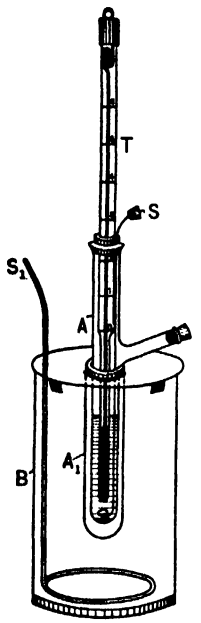

Fig. 88

In carrying out a determination with the Beckmann apparatus, a weighed quantity of solvent is placed in A, and the temperature of the refrigerating mixture is regulated so as to be not more than 5° below the freezing-point of the solvent. The tube A is removed from its jacket, and is immersed in the freezing mixture until the solvent begins to freeze. It is then replaced in the jacket A_1, and the solvent is vigorously stirred. The temperature rises during the stirring until the true freezing-point is reached, after which it remains constant. This temperature is taken as the freezing-point of the solvent. The tube A is now removed from the freezing mixture, and a weighed amount of the substance whose molecular weight is to be determined is introduced. When the substance has dissolved, the tube is replaced in A_1 and the solution cooled not more than a degree below its freezing-point. A small fragment of the solid solvent is dropped into the solution, which is then stirred vigorously until the thermometer remains constant. The maximum temperature is taken as the freezing-point of the solution. The difference between the freezing-points of solution and solvent is the depression sought.

In order to obtain trustworthy results with the freezing-point method, it is necessary that only the pure solvent separate out when the solution freezes, and that excessive overcooling be avoided. When too great overcooling occurs, the subsequent freezing of the solution results in the separation of so large an amount of solvent in the solid state, that the observed freezing-point corresponds to the equilibrium temperature of a more concentrated solution than that originally prepared.

If the overcooling of the solution in degrees be represented by u, the heat of fusion of 1 gram of solvent at the freezing-point by

L_f, and the specific heat of the solvent by c, then the fraction of the solvent which will solidify, f, may be calculated by the formula,

$$f = \frac{cu}{L_f}. \tag{32}$$

When water is used as the solvent, $c = 1$ and $L_f = 80$. Therefore, for every degree of overcooling, the fraction of the solvent separating as ice will be 1/80, and the concentration of the original solution is increased by just so much. It is simpler, however, to apply the correction directly to the freezing-point depression instead of to the concentration.

The foregoing method for the measurement of freezing-points is sufficiently accurate for all ordinary laboratory requirements, where a precision not greater than 0.001° in the measurement of temperature is required. For precise measurements, however, the following conditions are essential: — (1) Rapid and certain attainment of the equilibrium temperature; (2) accurate measurement of the equilibrium temperature, preferably by means of a differential method in which the freezing-point depression is measured directly; and (3) exact determination of the concentration of the solution when equilibrium is attained. Numerous forms of apparatus have been designed with a view to meeting these conditions, but none is superior to that devised by Adams.* In this form of apparatus the above requirements were satisfied as follows: — (1) By thoroughly mixing the solution with a large amount of finely crushed ice by means of an efficient stirrer; (2) by measuring directly the freezing-point depression by means of a multiple-junction thermoelement and sensitive potentiometer; and (3) by analyzing the equilibrium solution by means of special optical apparatus with which the concentration could be determined with an accuracy of two parts of solute in a million of solvent.

A diagram of the apparatus is shown in Fig. 89. Two similar vacuum-jacketed cylinders, A and B, are completely surrounded with crushed ice contained in a large felt-covered tank. The cylinder A contains about 400 grams of ice and 600 grams of water, while the cylinder B contains the same respective amounts of ice and solution. The liquid in each cylinder is thoroughly mixed by means of the stirrers, S,S, which, when moved by the glass rods, R,R, pump liquid from the bottom of each jar and

* Jour. Am. Chem. Soc., 37, 481 (1915).

discharge it over the ice. The difference in temperature between the contents of A and B is measured directly by means of the thermo-element T. When equilibrium is attained, a sample for analysis is withdrawn by means of P, which also serves to introduce both water and solution into B.

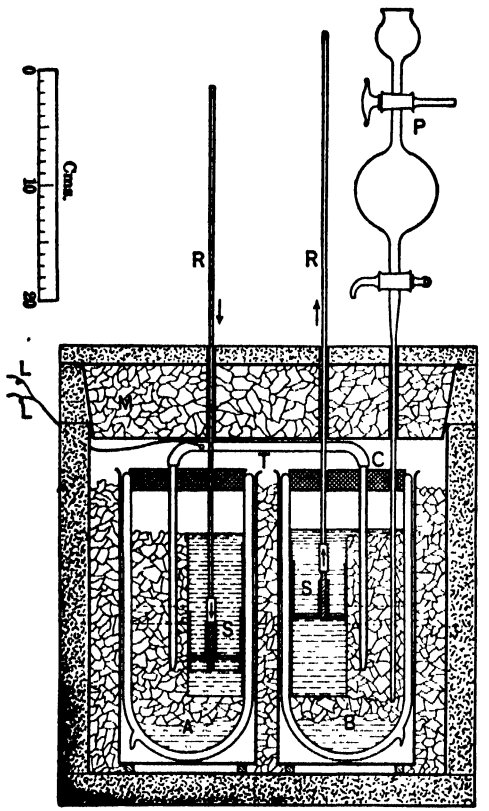

Fig. 89

The following table gives the results of a series of determinations of the freezing-points of solutions of mannite made with the Adams apparatus.

The third column contains the calculated values of the freezing-point depression, while the last column gives the concentrations calculated from the observed freezing-point depressions. It will be seen that the solution follows the freezing-point law very closely, i.e., the depression of the freezing-point is directly proportional to the concentration.

FREEZING-POINTS OF AQUEOUS SOLUTIONS OF MANNITE*

Concentration Millimols per 1000 gm. H_2O. $N \times 10^3$	Freezing-Point Depression		$N \times 10^3$ (calc.)
	dTf (obs.)	dTf (calc.)	
4.02	0.0075	0.0075	4.04
8.42	0.0157	0.0156	8.45
14.04	0.0260	0.0261	13.99
28.29	0.0525	0.0525	28.26
62.59	0.1162	0.1162	62.58

* Adams, loc. cit.

Molecular Weight in Solution. As has been pointed out, the molecular weight of a dissolved substance can be readily calculated provided that the osmotic pressure of a dilute solution of known, concentration at known temperature is determined. But the experimental difficulties attending the direct measurement of osmotic pressure are so great, that it is customary to employ other methods based upon properties of dilute solutions which are proportional to osmotic pressure. We have shown that in dilute solutions osmotic pressure is directly proportional, (1) to the relative lowering of the vapor pressure, (2) to the elevation of the boiling-point, and (3) to the depression of the freezing-point.

From this it follows, that *equimolecular quantities of different substances dissolved in equal volumes of the same solvent, exert the same osmotic pressure, and produce the same relative lowering of vapor pressure, the same elevation of boiling-point, and the same depression of freezing-point. Since equimolecular quantities of different substances contain the same number of molecules, it is evident that the magnitudes of osmotic pressure, relative lowering of vapor pressure, elevation of boiling-point and depression of freezing-point, are dependent upon the number of dissolved units present in the solution and are independent of their nature.*

It has been pointed out by Nernst that any process which involves the separation of solvent from solute, may be employed for the determination of molecular weights. A little reflection will convince the reader that the four methods discussed in this chapter involve such separation. Both van't Hoff and Raoult emphasized the fact that the formulas derived for the determination of molecular weights in solution depend upon assumptions which are valid *only* for dilute solutions. It follows, therefore, that *we are not justified in applying these formulas to concentrated solutions.* Up to the present time we have no satisfactory theory of concentrated solutions, neither can we state up to what concentration the gas laws apply.

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Solubility. J. H. Hildebrand. A. C. S. Monograph.

PROBLEMS

1. At 10° C., the osmotic pressure of a solution of urea is 500 mm. of mercury. If the solution is diluted to ten times its original volume, what is the osmotic pressure at 15° C.? *Ans.* 50.89 mm.

2. The osmotic pressure of a solution of 0.184 gram of urea in 100 cc. of water was 56 cm. of mercury at 30° C. Calculate the molecular weight of urea. *Ans.* 62.12.

3. At 24° C. the osmotic pressure of a cane sugar solution is 2.51 atmospheres. What is the concentration of the solution in mols per liter?

4. At 25°.1 C. the osmotic pressure of a solution of glucose containing 18 grams per liter was 2.43 atmospheres. Calculate the numerical value of the constant R, when the unit of energy is the gram-centimeter.

5. The vapor pressure of ether at 20° C. is 442 mm. and that of a solution of 6.1 grams of benzoic acid in 50 grams of ether is 410 mm. at the same temperature. Calculate the molecular weight of benzoic acid in ether. *Ans.* 124.

6. At 10° C. the vapor pressure of ether is 291.8 mm. and that of a solution containing 5.3 grams of benzaldehyde in 50 grams of ether is 271.8 mm. What is the molecular weight of benzaldehyde?

7. A solution containing 0.5042 gram of a substance dissolved in 42.02 grams of benzene boils at 80°.175 C. Find the molecular weight of the solute, having given that the boiling-point of benzene is 80°.00 C., and its heat of vaporization is 94 calories per gram. *Ans.* 181.9.

8. A solution containing 0.7269 gram of camphor (mol. wt. = 152) in 32.08 grams of acetone (boiling-point = 56°.30 C.) boiled at 56°.55 C. What is the molar elevation of the boiling-point of acetone? What is its heat of vaporization? *Ans.* $K_b = 1.67$; $L_v = 129.5$ cals. per gram.

9. A solution of 9.472 grams of CdI_2 in 44.69 grams of water boiled at 100°.303 C. The heat of vaporization of water is 536 calories per gram. What is the molecular weight of CdI_2 in the solution? What conclusion as to the state of CdI_2 in solution may be drawn from the result?

10. The freezing-point of pure benzene is 5°.440 C. and that of a solution containing 2.093 grams of benzaldehyde in 100 grams of benzene is 4°.440 C. Calculate the molecular weight of benzaldehyde in the solution. K_f for benzene is 5.12. *Ans.* 104.6.

11. A solution of 0.502 gram of acetone in 100 grams of glacial acetic acid gave a depression of the freezing-point of 0°.339 C. Calculate the molar depression for glacial acetic acid. *Ans.* 3.9.

12. By dissolving 0.0821 gram of m-hydroxybenzaldehyde ($C_7H_6O_2$) in 20 grams of naphthalene (melting-point 80°.1 C.) the freezing-point is lowered by 0°.232 C. Assuming that the molecular weight of the solute is normal in the solution, calculate the molar depression for naphthalene and the heat of fusion per gram.

Ans. $K_f = 6.90$; $L_f = 36.2$ cals. per gram.

13. The density of benzene at its melting point is 0.8943, and its heat of fusion is 30.08 calories per gram. The melting point, 5.4° C., is lowered 0.54° by the addition of phenol. Calculate the osmotic pressure of the solution at 5.4° C. and also its concentration.

Ans. 2.15 atmos., 0.986 gm. per 100 gm. benzene.

14. The depression of the freezing point of a 1.9488 molal solution of KCl in water is 6.37° C. The heat of fusion for water is 1435.5 calories per mol at 0° C., and the difference in the molecular heat capacities of ice and water is 9.04. Having given that the vapor pressure of water at 20° C. is 17.539 mm., calculate the vapor pressure of the solution of potassium chloride. *Ans.* 16.485 mm.

CHAPTER IX

SOLUTIONS OF ELECTROLYTES

Abnormal Solutes. As has already been pointed out, the acceptance of Avogadro's hypothesis was greatly retarded by the discovery of certain substances whose vapor densities were abnormal. Thus, the vapor density of ammonium chloride is approximately one-half of that required by the formula NH_4Cl, while the vapor density of acetic acid corresponds to a formula whose molecular weight is greater than that calculated from the formula, $C_2H_4O_2$. The anomalous behavior of ammonium chloride and kindred substances has been shown to be due, not to a failure of Avogadro's law, but to a breaking down of the molecules — a process known as *dissociation*. The abnormally large molecular weight of acetic acid on the other hand, has been ascribed to a process of aggregation of the normal molecules, known as *association*. In extending the gas laws to dilute solutions similar phenomena have been encountered.

Association in Solution. When the molecular weight of acetic acid in benzene is determined by the freezing-point method, the depression of the freezing-point is abnormally small and consequently, the molecular weight will be greater than that corresponding to the formula, $C_2H_4O_2$. Acetic acid in benzene solution is thus shown to be associated. Almost all compounds containing the hydroxyl and cyanogen groups when dissolved in benzene are found to be associated. Solvents, such as benzene and chloroform, are frequently termed associating solvents, although it is doubtful whether they exert any positive associating action. There is considerable experimental evidence to show that those substances whose molecules are associated in benzene and chloroform solution, are also associated in the free condition. Just as the depression of the freezing-point of a solution of an associated substance is abnormally small, so its osmotic pressure and other related properties will be less than the calculated values.

Dissociation in Solution. Van't Hoff* pointed out that the osmotic pressures of solutions of most salts, of all strong acids, and of all strong bases are much greater for all concentrations than would be expected from the osmotic pressures of solutions of substances, like cane sugar or urea, for corresponding concentrations. Although van't Hoff was unable to offer any satisfactory explanation of this anomaly, he showed that the fundamental equation, $PV = RT$, would still hold, provided an empirical factor, i, were introduced and the equation written in the form,

$$PV = iRT. \tag{1}$$

It was originally believed that the factor, i, was a constant, but subsequently, when Arrhenius had advanced his theory of electrolytic dissociation, it became apparent that i must increase as the concentration diminishes. If the osmotic pressure of some substance, like cane sugar, which behaves normally, be represented by P_0, the factor i can be calculated by means of the expression,

$$i = \frac{P}{P_0}, \tag{2}$$

where P is the osmotic pressure of an abnormal solute at the same concentration. Since the osmotic pressure of a solution is proportional to the relative lowering of its vapor pressure, to the elevation of its boiling-point, and to the lowering of its freezing-point, it follows that any one of these colligative properties may be similarly employed to calculate the value of the empirical factor, i. A more definite conception of the abnormal behavior of salts will be gained by an inspection of the following table giving the values of the molar freezing-point depressions of four typical salts together with the corresponding values of i. The headings of the columns show the number of equivalents of solute dissolved in 1000 grams of water.

As we have learned in the preceding chapter, the formal freezing-point depressions of dilute solutions of normal solutes is constant and, in the case of aqueous solutions, its value is 1.86°. Inspection of the following table reveals the fact that the values of the molar freezing-point depressions of the four salt solutions are all greater than those of solutions of normal solutes, such as

* Zeit. phys. Chem., 1, 501 (1887).

VALUES OF MOLAR FREEZING-POINT DEPRESSIONS*

Concentration		0.005	0.006	0.01	0.02	0.05	0.1	0.2	0.5
KCl	dT_f/N	3.648	3.640	3.610	3.564	3.502	3.451	3.394	3.314
	i	1.963	1.959	1.943	1.918	1.885	1.861	1.833	1.800
K_2SO_4	dT_f/N	5.308	5.282	5.198	5.040	4.776	4.568	4.324	3.948
	i	2.857	2.843	2.798	2.713	2.570	2.459	2.333	2.316
$MgSO_4$	dT_f/N	3.148	3.112	3.006	2.854	2.638	2.460	2.270	2.008
	i	1.694	1.675	1.618	1.536	1.420	1.324	1.223	1.084
$K_3Fe(CN)_6$	dT_f/N	6.840	6.810	6.696	6.192	.....	.....	.....	.....
	i	3.681	3.665	3.604	3.333	.....	.....	.....	.....

* Noyes and Falk, Jour. Am. Chem. Soc., 32, 1011 (1910).

cane sugar or mannite. Furthermore, it will be seen that as the solutions are diluted, their molar depressions approach limiting values which are simple multiples of the normal depression, 1.86°. Thus, with solutions of KCl and $MgSO_4$, the molar depression approaches the value $3.72° = 2 \times 1.86°$, as the solutions are diluted, while with solutions of K_2SO_4 and $K_3Fe(CN)_6$ the respective limits toward which their formal depressions tend are $5.58° = 3 \times 1.86°$ and $7.44° = 4 \times 1.86°$. The preceding examples being typical of the behavior of all solutions in which the solute is an acid, a base or a salt, we may formulate the following generalization: — *The molar freezing-point depressions of dilute aqueous solutions of all abnormal solutes (acids, bases and salts) are greater than the corresponding depressions of solutions of normal solutes, and in every case, as the solutions are diluted, these depressions approach limiting values, which are simple multiples of the normal depression,* 1.86°.

These facts together with numerous other properties of dilute solutions of acids, bases and salts find their most satisfactory explanation in the theory of electrolytic dissociation.

The Theory of Electrolytic Dissociation. In 1887, Arrhenius* advanced an hypothesis to account for the abnormal osmotic activity of solutions of acids, bases and salts. He pointed out that just as the exceptional behavior of certain gases has been completely reconciled with the law of Avogadro, by assuming a dissociation of the vaporized molecule into two or more simpler molecules, so the enhanced osmotic pressure and the abnormally

* Zeit. phys. Chem., 1, 631 (1887).

great freezing-point depressions of solutions of acids, bases and salts can be explained, if we assume a similar process of dissociation. He proposed, therefore, that aqueous solutions of acids, bases and salts be considered as dissociated, to a greater or less extent, into positively- and negatively-charged particles or *ions*, and that the increase in the number of dissolved units due to this dissociation is the cause of the enhanced osmotic activity. According to this hypothesis, hydrochloric acid, potassium hydroxide and potassium chloride, when dissolved in water, dissociate in the following manner: —

$$HCl \rightleftarrows H^{\cdot} + Cl'$$
$$KOH \rightleftarrows K^{\cdot} + OH'$$
$$KCl \rightleftarrows K^{\cdot} + Cl',$$

where the dots indicate positively-charged ions and the dashes negatively-charged ions. The reversed arrows indicate that a definite equilibrium exists between the ions and the undissociated molecules, a certain number of undissociated molecules always being present at finite concentrations. As the solution is diluted, the percentage of undissociated molecules steadily decreases, and ultimately, when the solution becomes infinitely dilute, the solute is completely dissociated.

In each of the above cases, one molecule yields two ions, so that, if dissociation is complete, the maximum osmotic effect should not be greater than twice that produced by an equimolecular quantity of a substance which behaves normally. Reference to the preceding table shows that the value of i for potassium chloride approaches the limiting value of 2 as the solution is diluted. The other salts given in the table dissociate, according to Arrhenius, in the following manner: —

$$K_2SO_4 \rightleftarrows 2\,K^{\cdot} + SO_4'',$$
$$MgSO_4 \rightleftarrows Mg^{\cdot\cdot} + SO_4'',$$
$$K_3Fe(CN)_6 \rightleftarrows 3\,K^{\cdot} + Fe(CN)_6'''.$$

If these equations correctly represent the process of dissociation, then when dissociation is complete, the osmotic effect of infinitely dilute solutions of potassium sulphate should be three times that produced by an equimolar concentration of a normal solute, while in the case of an infinitely dilute solution of potassium ferri-cyanide, the effect should be four times that of a normal solute. On

referring to the table, it will be seen that the limiting values of i for each of the salts, KCl, K_2SO_4, $MgSO_4$ and $K_3Fe(CN)_6$, are 2, 3, 2 and 4 respectively. In other words, the factor, i, may be regarded as representing the number of dissolved units resulting from one formula-weight of solute. It is because of this significance which attaches to i that it is sometimes called the *mol-number* of the solute.

The theory of electrolytic dissociation, or electrolytic ionization as it is frequently called, enables us to calculate the degree of ionization in any solution by comparing its freezing-point depression with the freezing-point lowering of an equimolecular solution of a normal substance.

Let us suppose that the degree of dissociation of 1 mol of a dissolved substance is α, each molecule yielding n ions. Then the number of undissociated mols will be $1 - \alpha$, and the total number of dissolved units will be

$$1 - \alpha + n\alpha.$$

If dT_f is the depression of the freezing-point produced by the substance, and dT_{0f} the depression produced by an equimolecular quantity of an undissociated substance, then

$$\frac{1 - \alpha + n\alpha}{1} = \frac{dT_f}{dT_{0f}} = i,$$

or

$$\alpha = \frac{i - 1}{n - 1}. \tag{3}$$

It will be observed that this formula is identical with that derived for the degree of dissociation of a gas (p. 43). If this formula be applied to the freezing-point data for solutions of potassium chloride given in the preceding table, the percentage dissociation at the different dilutions given in the following table are obtained.

The figures in the last column show that the degree of dissociation increases as the concentration diminishes.

It was further pointed out by Arrhenius that all of the substances which exhibit abnormal osmotic effects, when dissolved in water, yield solutions which conduct the electric current, whereas, aqueous solutions of such substances as cane sugar, urea and alcohol, exert normal osmotic pressures, but do not conduct electricity any better than the pure solvent. In other words, only

electrolytes* are capable of undergoing ionic dissociation; hence Arrhenius termed the hypothesis the *electrolytic dissociation theory.*

PERCENTAGE DISSOCIATION OF SOLUTIONS OF POTASSIUM CHLORIDE

Conc., *N.*	dT_f/N	i	α
0.005	3.648	1.963	0.963
0.006	3.640	1.959	0.959
0.01	3.610	1.943	0.943
0.02	3.564	1.918	0.918
0.05	3.502	1.885	0.885
0.1	3.451	1.861	0.861
0.2	3.394	1.833	0.833
0.5	3.314	1.800	0.800

As we have seen, when potassium chloride is dissolved in water, it is supposed to dissociate into positively-charged potassium ions and negatively-charged chlorine ions. Accordingly when two platinum electrodes, one charged positively and the other negatively, are introduced into the solution, the potassium ions move toward the negative electrode and the chlorine ions move toward the positive electrode, the passage of a current through the solution consisting in the ionic transfer of electric charges. Since the undissociated molecules are electrically neutral and hence do not participate in the transfer of electric charges, it follows that the conductance of a solution of an electrolyte is dependent upon the degree of dissociation. The relation between electrical conductance and the degree of ionization will be discussed in a subsequent chapter. It may be stated at this point, however, that the values of α, based upon measurements of electrical conductance, while showing some discrepancies in individual cases, are in general in good agreement with the values obtained by the freezing-point method.

Dissociation and Lowering of Vapor Pressure. The lowering of the vapor pressure of water produced by dissolved potassium

* The term *electrolyte* strictly refers to the solution of an ionized substance, although it is often applied to acids, bases and salts because, when dissolved, they produce electrolytes. To avoid confusion, the term "*ionogen*" (ion former) has been proposed for those substances which give conducting solutions.

chloride has been accurately determined by Lovelace, Frazer and Sease.* The following table contains a summary of their results, together with the vapor pressure lowerings for solutions of mannite of equal concentrations.

PERCENTAGE DISSOCIATION OF DILUTE SOLUTIONS OF POTASSIUM CHLORIDE CALCULATED FROM VAPOR PRESSURE LOWERINGS

Formal Concentration	$p_1 - p_2$ for KCl	$p_1 - p_2$ for Mannite	Percentage Dissociation		
			V. P. (20°)	Cond. (18°)	F.-P.
0.05	0.0294	0.0156	0.885	0.889	0.885
0.10	0.0574	0.0311	0.846	0.860	0.861
0.20	0.1128	0.0622	0.814	0.827	0.833
0.30	0.1680	0.0934	0.799	.....	.....
0.40	0.2225	0.1243	0.790	.....	.....
0.50	0.2785	0.1555	0.790	0.779	0.800

By dividing the vapor pressure lowerings of the potassium chloride solutions by the corresponding lowerings of the mannite solutions, the values of the mol-number, i, are obtained, and on substituting the resulting values of i in equation (3), the degree of dissociation given in the fourth column of the table can be calculated. The resulting values of the degree of dissociation will be seen to be in fairly close agreement with those derived from conductivity and freezing-point measurements.

Classification of Electrolytes. Electrolytes may be classified according to the extent to which they undergo ionization in solution. Those electrolytes which are largely dissociated in dilute solutions are commonly known as *strong electrolytes*, whereas those which are only slightly dissociated are called *weak electrolytes*. All of the stronger acids and bases and nearly all salts belong to the class of strong electrolytes.

Electrolytes may also be classified according to the character of the ions which they yield in solution. Thus, such substances as HCl, KOH, and KCl, which yield on dissociation two singly charged ions, are called *uni-univalent* electrolytes, while such substances as H_2SO_4, $Ca(OH)_2$ and $CaCl_2$, which dissociate into

* Jour. Am. Chem. Soc., 43, 119 (1921).

one doubly and two singly charged ions are termed *uni-bivalent* electrolytes. Similarly, electrolytes such as $CuSO_4$ and $MgSO_4$, which yield two doubly charged ions, are *bi-bivalent*, and $K_3Fe(CN)_6$, which dissociates into one trebly, and three singly charged ions, is *uni-trivalent*.

Intermediate and Complex Ions. Electrolytes which yield more than two ions when completely dissociated, probably undergo ionization in two different ways, giving rise to so-called *intermediate ions*. For example, in extremely dilute solutions of sulphuric acid, dissociation takes place according to the equation,

$$H_2SO_4 \rightleftarrows 2\,H^{\cdot} + SO_4''.$$

In more concentrated solutions, however, a portion of the acid dissociates as above, and another portion undoubtedly dissociates according to the equation,

$$H_2SO_4 \rightleftarrows H^{\cdot} + HSO_4',$$

giving rise to the intermediate ion, HSO_4'. While in the case of sulphuric acid, the concentration of the intermediate ion can be determined,* we have as yet no satisfactory method for estimating the extent to which intermediate ions are formed. It is, therefore, manifestly impossible to determine the degree of ionization in solutions of electrolytes which are capable of yielding intermediate ions, except at extremely small dilutions.†

Many electrolytes exhibit a tendency to combine with other electrolytes in solution to form complex compounds. When these complex compounds dissociate, they give rise to *complex ions*. For example, if a solution of silver nitrate is treated with an excess of potassium cyanide, a reaction represented by the following equation occurs: —

$$2\,KCN + AgNO_3 = KNO_3 + KAg(CN)_2.$$

The resulting complex electrolyte dissociates according to the equation,

$$KAg(CN)_2 \rightleftarrows K^{\cdot} + Ag(CN)_2',$$

giving rise to the complex ion, $Ag(CN)_2'$.

Properties of Completely Ionized Solutions. The chemical properties of an ion are very different from the properties of the

* See Noyes and Stewart, Jour. Am. Chem. Soc., 32, 1133 (1910).

† See Hall and Harkins, ibid. 38, 2672 (1916).

atom or radical when deprived of its electrical charge. For example, the sodium ion is present in an aqueous solution of sodium chloride, but there is no evidence of chemical reaction with the solvent; whereas, the element in the electrically-neutral condition reacts violently with water, evolving hydrogen and forming a solution of sodium hydroxide. Again, take the element chlorine: when chlorine in the molecular condition, either as gas or in solution, is added to a solution of silver nitrate, no precipitate of silver chloride is formed. Furthermore, chlorine in such compounds as $CHCl_3$, CCl_4, etc., is not precipitated by silver nitrate, since these compounds are not dissociated by water. Or, chlorine may be present in a compound which is dissociated by water and yet not exhibit its characteristic reactions, because it is present in a complex ion. Thus, potassium chlorate dissociates in the following manner: —

$$KClO_3 \rightleftarrows K^{\cdot} + ClO'_3.$$

On adding silver nitrate, there is no precipitation, because the chlorine forms a complex ion with oxygen.

The physical properties of completely ionized solutions are, in general, additive. This is well illustrated by a series of solutions of colored salts, the color of which is due to the presence of a particular ion. It is found, when the solutions are sufficiently dilute to insure complete dissociation, that they all have the same color. The additive character of the colors of solutions of electrolytes is brought out in a striking manner by a comparison of their absorption spectra. Ostwald* photographed the absorption spectra of solutions of the permanganates of lithium, cadmium, ammonium, zinc, potassium, nickel, magnesium, copper, hydrogen and aluminium, each solution containing 0.002 gram-equivalents of salt per liter. The absorption spectra, as shown in Fig. 90, will be seen to be practically identical, the bands occupying the same position in each spectrum. This affords a strong confirmation of the theory of electrolytic dissociation, according to which a dilute solution is to be regarded as a mixture of electrically equivalent quantities of oppositely charged ions, each of which contributes its specific properties to the solution. The permanganate ion being colored, and common to all of the salts examined, and the positive ions of the various substances being colorless,

* Zeit. phys. Chem., 9, 579 (1892).

it follows that when dissociation is complete, the absorption spectra of all of the solutions must be identical.

It should be pointed out that subsequent investigations by Hantzsch,* and others, on the relation of the light-absorbing power of solutions of electrolytes to their degree of ionization, have shown that no satisfactory explanation of the mechanism of the phenomenon can be adduced unless we adopt the view that absorption is independent of ionization. According to Ostwald,† the blue color of very dilute solutions of cupric chloride is due to the presence of $Cu^{\cdot\cdot}$ ions, whereas the color of the more concentrated solutions is due to the presence of both ions and undissociated molecules, the yellow color of the latter together with the blue color of the former, causing the solution to appear green. This seemingly satisfactory and simple hypothesis is open to several objections, among which may be mentioned its failure to account for the presence of complex anions containing copper, which subsequent investigations have proved to be present in concentrated solutions.

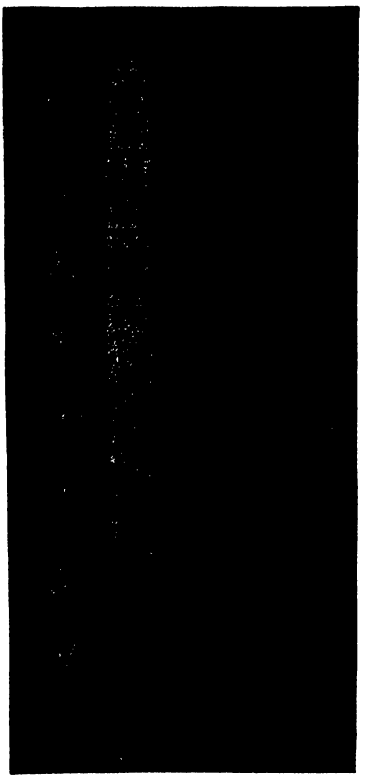

Fig. 90

In a recent spectrophotometric study of the absorption of light by solutions of cupric chloride, the author‡ has furnished experimental evidence which appears to justify the following conclusions:

* Hantzsch, Ber. deutsch. chem. Ges., 41, 1216, 4328 (1908); Zeit. phys. Chem., 63, 373 (1908); 72, 362 (1910).

† Ostwald, Lehrbuch der allgemeinen Chemie, 1, 799.

‡ Getman, Jour. Phys. Chem., 26, 217 (1922).

(1) Complex anions containing copper exist in concentrated solutions of cupric chloride.

(2) The substitution of a chlorine atom for a water molecule in any complex ion, displaces the absorption toward the red end of the spectrum.

(3) Increase in concentration, rise in temperature, or the addition of solutions of colorless chlorides, cause a displacement of the absorption maximum of cupric chloride toward the red end of the spectrum.

Of the various hypotheses which have been advanced in explanation of the change in color of cupric chloride solutions, that involving the assumption of complex ions seems to be in closest accord with all of the facts. Thus, in extremely dilute solutions, we may consider dissociation as taking place in the following manner:

$$CuCl_2 + 4\,H_2O \rightarrow \left[\begin{matrix} H_2O \\ H_2O \end{matrix}\!\!>\!Cu\!<\!\!\begin{matrix} H_2O \\ H_2O \end{matrix}\right]^{\cdot\cdot} + 2\,Cl''.$$

On the other hand, in very concentrated solutions, the processes of dissociation and complex formation may be formulated as follows:

$$2\,CuCl_2 + 4\,H_2O \rightarrow \underbrace{\left[\begin{matrix} H_2O \\ H_2O \end{matrix}\!\!>\!Cu\!<\!\!\begin{matrix} H_2O \\ H_2O \end{matrix}\right]^{\cdot\cdot}}_{\text{blue}} + \underbrace{\left[\begin{matrix} Cl \\ Cl \end{matrix}\!\!>\!Cu\!<\!\!\begin{matrix} Cl \\ Cl \end{matrix}\right]''}_{\text{yellow}}$$

$$\underbrace{\qquad\qquad\qquad\qquad}_{\text{green}}$$

In solutions of intermediate concentrations, other ions may exist in which the water groups of the fully hydrated copper ion are partially replaced by chlorine atoms. Not only is this hypothesis in agreement with the experimental facts, but also it is in accord with the law of mass action. Furthermore, it is known that non-aqueous solutions of cupric chloride, although differing as to their absorption spectra, behave in other respects quite similarly to aqueous solutions. This fact would seem to meet the further criticism of the complex ion hypothesis, that the presence of complex ions renders it difficult to account for changes in the absorption spectrum occurring with change in solvent.

For example, when cupric chloride is crystallized from its solution in pyridine, it separates as a blue salt having the formula, $CuCl_2.2\,C_6H_5N$, which will be seen to be the analogue of the salt $CuCl_2.2H_2O$, obtained from aqueous solution. It is more than probable, therefore, that complex ions containing pyridine exist in pyridine solutions which are entirely analogous to the hydrated ions occurring in aqueous solutions. In fact, if we accept Werner's view of the interdependence of dissociation and solvation, we must regard all cations in dilute salt solutions as consisting of metallic atoms combined with as many molecules of the solvent as correspond to the coördination number of the metal.

A number of other properties of completely dissociated solutions have been shown to be additive. Among these may be mentioned density, specific refraction, surface tension, thermal expansion, and magnetic rotatory power. Additional evidence in favor of the theory of electrolytic dissociation will be furnished in forthcoming chapters. Notwithstanding the large number of facts which can be satisfactorily interpreted by the theory, there are directions in which it requires amplification and modification.

Hydration. Attention has already been directed to the fact, that the lack of agreement between the observed and calculated value of the osmotic pressures of concentrated solutions of cane sugar can be satisfactorily explained by assuming that each molecule of sugar forms a pentahydrate through the removal of five molecules of water from the solvent. Additional evidence of the existence of hydrates of cane sugar in aqueous solution has been furnished by Jones and the author* from freezing-point data, by Scatchard† from calculations based on vapor pressure measurements, and also by Philip‡ from measurements of the solubility of hydrogen in sucrose solutions. The average degree of hydration of sugar, as calculated by Scatchard from various available sources, is represented graphically in Fig. 91. The results

* Am. Chem. Jour., **32**, 327 (1904).

† Jour. Am. Chem. Soc., **43**, 2406 (1921).

‡ Jour. Chem. Soc., **99**, 711 (1907).

obtained by each of the different methods appear to agree within the limits of their respective experimental errors and to confirm the existence of a definite hydrate of cane sugar in aqueous solution.

That the phenomenon of hydration is not confined to non-electrolytes has been shown by Jones and his students* who have measured the depression of the freezing-point of water produced by

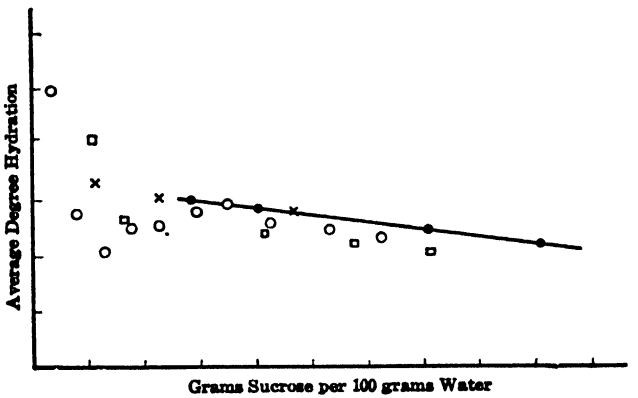

Fig. 91

Full line: Hydration from vapor pressure at 0°.
Circles: " " freezing-point, Jones and Getman, recalculated by Scatchard.
Crosses: " " solubility of hydrogen at 8°, calculated by Philip.
Squares: " " osmotic pressure at 0°, Berkeley, calculated by Porter.

a large number of electrolytes in very concentrated solutions. Dissociation of electrolytes in aqueous solution increases with the dilution, becoming complete at a concentration of about 0.001 molar. We should expect the dissociation to diminish with increasing concentration, until, if the electrolyte is sufficiently soluble, the depression of the freezing-point becomes normal. Investigations by Jones and his co-workers† have shown that the facts are contradictory to this expectation. They found that the value of the molecular depression of the freezing-point of water produced by a number of electrolytes, diminishes with in-

* Publ. No. 60, Carnegie Institution.

† Am. Chem. Jour. 22, 5, 110 (1899); 23, 89 (1900).

creasing concentration up to a certain point, as would be expected, and then increases again. This is illustrated by the freezing-point curves for several typical chlorides shown in Fig. 92. The increase in the molecular depression becomes very marked at great concentrations; in fact, the molecular depression in a molar solution is frequently greater than the molar depression corresponding to a completely dissociated salt. This phenomenon, which has been found to be quite general, may be accounted for by assuming that the dissolved substance has entered into combination with a portion of the water, thus removing it from the rôle of solvent. A molecular complex formed by the union of one molecule of solute and a number of molecules of water, will act as a single dissolved unit in depressing the freezing-point of the pure solvent. Evidently the total amount of water present, which functions as solvent, will be diminished by the amount of water which has been appropriated by the solute.

If hydrates exist in aqueous solution, then those solutes which exhibit the greatest depressing action on the freezing-point of water, should be the ones which crystallize from the solution with the greatest amount of water of crystallization. That there is a relation between freezing-point depression and water of crystallization, is shown by the curves in Fig. 92. Those salts which crystallize without water of crystallization produce the least depression of the freezing-point. Those crystallizing with two molecules of water are next in order, and then follow those crystallizing with four and six molecules respectively. Similar relations are found to hold for the corresponding bromides, iodides and nitrates. We conclude, therefore, that those solutes which crystallize with the same amount of water produce approximately the same depression of the freezing-point of water.

While Jones was undoubtedly correct in attributing the observed abnormalities in the freezing-point depressions of concentrated solutions of electrolytes to the formation of hydrates, his method of calculating their approximate composition was wholly erroneous and, in several cases, led to the absurd conclusion that all of the water present had entered into combination with the solute.

It is interesting to recall, that as long ago as 1893, Werner*

* Zeit. anorg. Chem., 3, 296 (1893).

expressed the view that when an electrolyte is dissolved in water, hydration of the solute precedes its dissociation, and, after ionic equilibrium has been established, the positive ion will hold in combination as many molecules of water as correspond to its

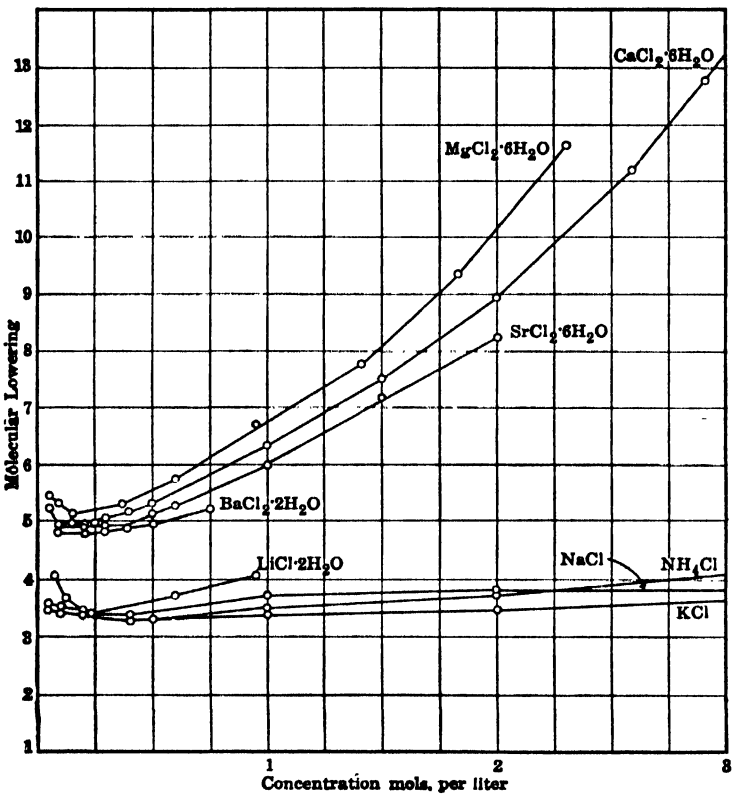

Fig. 92

coördination number. For example, cupric chloride may be considered to dissociate in dilute solution in the following manner: —

$$CuCl_2 + 4\,H_2O \rightleftarrows \left[\begin{matrix} H_2O \\ H_2O \end{matrix}\!\!\diagdown\!\!Cu\!\!\diagup\!\!\begin{matrix} H_2O \\ H_2O \end{matrix}\right]^{\cdot\cdot} + 2\,Cl'.$$

The copper ion, it will be observed, is assumed to be hydrated to the extent of four molecules of water, corresponding to its coör-

dination number, while the chlorine ion is assumed to remain unhydrated.

The assumption that the ions undergo hydration in solution has been confirmed experimentally, but discussion of these experiments must be deferred until a later chapter.

Without adducing further evidence in favor of the hydration hypothesis, it may be stated that its validity is quite generally accepted, although there are many problems connected with the hypothesis which still await solution.

According to the views which have just been outlined, when an electrolyte is dissolved in water, the molecules first become hydrated, and then dissociate into ions which are hydrated to the same or different degrees. For example, the dissociation of potassium chloride should be expressed by the equation,

$$\underset{\text{(solid)}}{KCl} + aq = \underset{\text{(solution)}}{KCl \,.\, aq} = [K\,(H_2O)_n]^{\cdot} + [Cl\,(H_2O)_{n'}]\,',$$

where the symbol aq denotes a large amount of water, and where n and n' denote the numbers of molecules of water which are associated with the two ions.

In the derivation of equation (3), expressing the relation between freezing-point depression and ionization, it was assumed that the solute was unhydrated. In view of the tendency of all electrolytes to become hydrated when dissolved, it follows that the values of the degree of ionization, calculated from freezing-point depressions, must be more or less erroneous. This question has been carefully considered by Noyes and Falk* who, after reviewing the best available experimental data, state that the degree of ionization of most uni-univalent strong electrolytes, in aqueous solutions whose concentrations are less than 0.1 molar, can be calculated from the freezing-point depressions of their solutions with an accuracy of from 1 to 4 per cent.

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Hydrates in Solution. Transactions of the Faraday Society. Vol. III (1907).

* loc. cit.

PROBLEMS

1. At 18° C. a 0.5 molar solution of NaCl is 74.3 per cent dissociated. What would be the osmotic pressure of the solution in atmospheres at 18° C.? *Ans.* 20.79.

2. The vapor pressure of water at 20° C. is 17.406 mm. and that of a 0.2 molar solution of potassium chloride is 17.296 mm. at the same temperature. Calculate the degree of dissociation of the salt. *Ans.* 75.38 per cent.

3. The degree of dissociation of a 0.5 molar solution of sodium chloride at 25° is 74.3 per cent. Calculate the osmotic pressure of the solution at the same temperature. *Ans.* 21.32 atmos.

4. A solution containing 1.9 mols of calcium chloride per liter exerts the same osmotic pressure as a solution of glucose containing 4.05 mols per liter. What is the degree of ionization of the calcium chloride? *Ans.* 56.6 per cent.

5. At 0° C. the vapor pressure of water is 4.620 mm. and of a solution of 8.49 grams of $NaNO_3$ in 100 grams of water 4.483 mm. Calculate the degree of ionization of $NaNO_3$. *Ans.* 67 per cent.

6. At 0° C. the vapor pressure of water is 4.620 mm. and that of a solution of 2.21 grams of $CaCl_2$ in 100 grams of water is 4.583 mm. Calculate the apparent molecular weight and the degree of ionization of $CaCl_2$. *Ans.* $M = 49.66$, $\alpha = 62$ per cent.

7. The boiling-point of a solution of 0.4388 gram of sodium chloride in 100 grams of water is 100°.074 C. Calculate the apparent molecular weight of the sodium chloride and its degree of ionization. $K_b = 0.518$. *Ans.* $M = 30.84$, $\alpha = 89.7$ per cent.

8. The boiling-point of a solution of 3.40 grams of $BaCl_2$ in 100 grams of water is 100°.208 C. $K_b = 0.518$. What is the degree of ionization of the $BaCl_2$? *Ans.* 72.5 per cent.

9. At 100° C. the vapor pressure of a solution of 6.48 grams of ammonium chloride in 100 grams of water is 731.4 mm. $K_b = 0.518$. What is the boiling-point of the solution? *Ans.* 101.09° C.

10. A solution of 1 gram of silver nitrate in 50 grams of water freezes at −0°.348 C. Calculate to what extent the salt is ionized in solution. $K_f = 1.86$. *Ans.* 59 per cent.

11. A solution of NaCl containing 3.668 grams per 1000 grams of water freezes at −0°.2207 C. Calculate the degree of ionization of the salt. $K_f = 1.86$. *Ans.* 89.2 per cent.

12. The freezing-point of a solution of barium hydroxide containing 1 mol in 64 liters is −0°.0833 C. What is the concentration of hydroxyl ions in the solution? Take $K_f = 1.86$ for concentrations in mols per liter. *Ans.* 0.0284 gm. − ion per liter.

13. The vapor pressure of water at 0° C. is 4.620 mm., and the lower-

ing of the vapor pressure produced by dissolving 5.64 grams of sodium chloride in 100 grams of water is 0.142 mm. What is the freezing-point of the solution? $K_f = 1.86$. *Ans.* $-3.177°$ C.

14. A solution containing 8.34 grams Na_2SO_4 per 1000 grams of water freezes at $-0°.280$ C. Assuming dissociation into 3 ions, calculate the degree of ionization and the concentrations of the $Na^{\cdot}$ and SO_4'' ions. $K_f = 1.86$. *Ans.* $\alpha = 78.2$ per cent; $Na = 0.0918$ gm. – ion per liter; $SO_4'' = 0.0459$ gm. – ion per liter.

CHAPTER X

COLLOIDS

Crystalloids and Colloids. In the course of his investigations on diffusion in solutions, Thomas Graham* drew a distinction between two classes of solutes, which he termed *crystalloids* and *colloids*. Crystalloids, as the name implies, can be obtained in the crystalline form: to this class belong nearly all of the acids, bases and salts. Colloids, on the other hand, are generally amorphous, such substances as albumin, starch and caramel being typical of the class. Because of the gelatinous character of many of the substances belonging to this class, Graham termed them colloids ($\kappa o\lambda\lambda\alpha$ = glue, and $\epsilon\iota\delta o\varsigma$ = form). The differences between the two classes are most apparent in the physical properties of their solutions. Crystalloids diffuse much more rapidly than colloids; thus, the velocity of diffusion of caramel is nearly 100 times slower than that of hydrochloric acid at the same temperature. While crystalloids exert osmotic pressure, lower the vapor pressure and depress the freezing-point of the solvent, colloids have very little effect upon the properties of the solvent. The marked difference between the rate of diffusion of crystalloids, on the one hand, and that of colloids, on the other, renders their separation comparatively easy.

If a solution containing both crystalloids and colloids be placed in a vessel over the bottom of which is stretched a colloidal membrane, such as parchment, and the whole be immersed in pure water, the crystalloids will pass through the membrane, while the colloids will be left behind. This process was termed by Graham, *dialysis*, while the apparatus employed to effect such a separation was called a *dialyzer*. When a solution of sodium silicate is added to an excess of hydrochloric acid, the products of the reaction, silicic acid and sodium chloride, remain in solution. When the mixture is placed in a dialyzer, the sodium chloride and the hydrochloric acid, being crystalloids,

* Phil. Trans. Roy. Soc., 151, 183 (1861).

diffuse through the membrane of the dialyzer, leaving behind the colloidal silicic acid.

The terms crystalloid and colloid, as used at the present time, have acquired different meanings from those assigned to them by Graham. The terms are now considered to refer, not so much to different classes of substances, as to different states which almost all substances can assume under certain conditions.

Disperse Systems. If in a two-component system, the size of the particles of one of the components be gradually reduced until its dimensions become microscopic or submicroscopic, we have what is known as a *disperse system.* The characteristic properties of disperse systems are attributable to the enormous surface of the dispersed phase. So-called "colloidal solutions" are in reality examples of such disperse systems.

Nomenclature. Graham distinguished between two conditions in which colloids were obtainable, the term *sol* being applied to forms in which the system resembled a liquid, while the term *gel* was used to designate those forms which were solid and jelly-like. When one of the components of the solution was water, the two forms were called a *hydrosol* and a *hydrogel.* In like manner, when alcohol was one of the components, the terms *alcosol* and *alcogel* were applied to the two forms.

As the knowledge of colloids has developed, it has become necessary to supplement Graham's nomenclature by the introduction of various other terms. It is known to-day that the essential difference between colloidal suspensions and solutions on the one hand, and true solutions on the other, is due to the difference in the degree of subdivision, or degree of *dispersion* of the dissolved substance. In a true solution, the dissolved substance is generally present either in the molecular or ionic condition, as may be shown by means of the familiar osmotic methods for molecular weight determination. In colloidal solutions, however, the degree of dispersion is not so great, it having been found to vary from above the limit of microscopic visibility, (1×10^{-5} cm.), to that of molecular dimensions, (1×10^{-8} cm.). When the degree of dispersion varies from 1×10^{-3} cm. to 1×10^{-5} cm., the particles are termed *microns.* The properties of the disperse phase at this degree of dispersion differ appreciably from the properties of the same substance when present in large masses. When the degree of dis-

persion lies between 1×10^{-5} cm. and 5×10^{-7} cm. the particles are known as *submicrons*. The existence of particles whose diameters are approximately 1×10^{-7} cm. has been demonstrated by Zsigmondy with the ultramicroscope by using these particles as nuclei for the formation of larger particles; these minute particles are termed *amicrons*. When the degree of dispersion is increased beyond this limit, all heterogeneity apparently vanishes, and we enter the realm of true solutions.

When the dispersion is not too great, colloidal solutions may be divided into *suspensions* and *emulsions*, according to whether the disperse phase is a solid or a liquid. As the dispersion is increased, we obtain suspension and emulsion colloids, which may be conveniently called *suspensoids* and *emulsoids*. Suspensoids and emulsoids are included under the general term, *dispersoids*. The classification of sols as suspensoids and emulsoids, however, is not entirely satisfactory. A better system is that in which the presence, or the absence, of affinity between the disperse phase and the dispersion medium is made the basis of classification. Where there is marked affinity between the two phases, the system is termed *lyophile*, and where such affinity is absent, the system is termed *lyophobe*. When the dispersion medium is water, the terms *hydrophile* and *hydrophobe* are employed.

In the reversible transformation of a sol into a gel, we are not warranted in referring to the change from gel to sol as an act of solution, for if the gel really dissolved, a solution and not a sol would result. Various terms have been proposed for these reversible transformations but perhaps the most satisfactory are the terms *gelation* and *solation*, the former designating the formation of a gel from a sol and the latter the reverse process.

The Ultramicroscope. When a narrow beam of sunlight is admitted into a darkened room, the dust particles in its path are rendered visible by the scattering of the light at the surface of the particles. If the air of the room is free from dust, no shining particles will be seen and the space is said to be "optically void." When the particles of dust are very minute, the beam of light acquires a bluish tint.

The luminosity of the path of a beam of light is known as the

Tyndall phenomenon and may be considered as an indication of the presence of suspended particles, provided the luminosity is not caused by fluorescence. Almost all colloidal solutions exhibit this phenomenon when a powerful beam of light is passed through them, thus proving the presence of discrete particles in the solutions.

The ultramicroscope is an instrument devised by Siedentopf and Zsigmondy* for the detection of colloidal particles much too small to be seen by the naked eye. A powerful beam of light, issuing from a horizontal slit, is brought to a focus within the colloidal solution under examination by means of a microscope objective, and this image is viewed through a second microscope, the axis of which is at right angles to the path of the beam.

When examined in this way, a colloidal solution usually appears to be swarming with minute particles, moving rapidly in a dark field; whereas a true solution, if properly prepared, appears optically void. With the ultramicroscope it is possible to count the number of particles present in a given volume of a colloidal solution. By means of a chemical analysis, the mass of colloid per unit of volume can be determined, and from this, the average mass of each particle can be calculated. If the particles be assumed to be spherical in shape and to have the same density as larger masses of the same substance, we can calculate the volume of a single particle, and from this its diameter. Thus, Burton† in his experiments on gold, silver and platinum sols, found the average diameter of the colloidal particles to range from 0.2 to 0.6 micron.

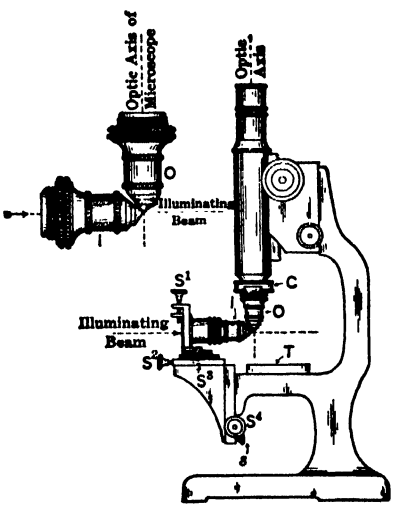


Fig. 93

* "Colloids and the Ultramicroscope," by R. Zsigmondy. Trans. by Alexander. John Wiley & Sons, Inc.

† Phil. Mag., 11, 425 (1906).

Zsigmondy's latest ultramicroscope, Fig. 93, consists of two compound microscopes placed at right angles, and having their objectives so cut away as to permit them to be brought very close together. A drop of the liquid to be examined is placed between the front lenses of the objectives where it is held by capillary attraction, thus doing away with the necessity for a cell as in the earlier form of instrument. Since the rays of light have only a short distance to travel, it is possible to examine dark as well as colorless liquids.

The ultramicroscopic character of lyophile sols is by no means sharply defined, notwithstanding the fact that they exhibit the Tyndall phenomenon. It has been suggested by Zsigmondy, that the lack of sharpness in definition observed with emulsoids is probably due to the relatively small difference between the refractive indices of the disperse phase and the dispersion medium. Where the difference between the refractive indices of the two phases is very great, as in the case of the metallic sols, excellent definition is obtained. It is of interest to note, that although the basic hydroxides are apparently suspensoids, yet in their ultramicroscopic characteristics they closely resemble lyophile sols.

Ultrafiltration. Almost all sols can be filtered through ordinary filter paper without undergoing more than a slight change in concentration, due to initial adsorption. The rate of filtration varies widely, depending upon the viscosity of the sol. As a general rule, lyophile sols filter more slowly than lyophobe sols, owing to the high viscosity of the former.

By filtering an arsenious sulphide sol through a porous earthenware filter, Linder and Picton* succeeded in obtaining four different sizes of particles which they described as follows: — (1) visible under the microscope, (2) exhibited the Tyndall phenomenon, (3) retained by porous plate, and (4) passed through porous plate unchanged. By employing plates of different degrees of porosity, and determining the average size of the pores which just permit filtration, it is possible to determine the size of the particles which constitute the disperse phase of a sol. If we make use of a series of graduated filters, prepared by impregnating filter paper with a

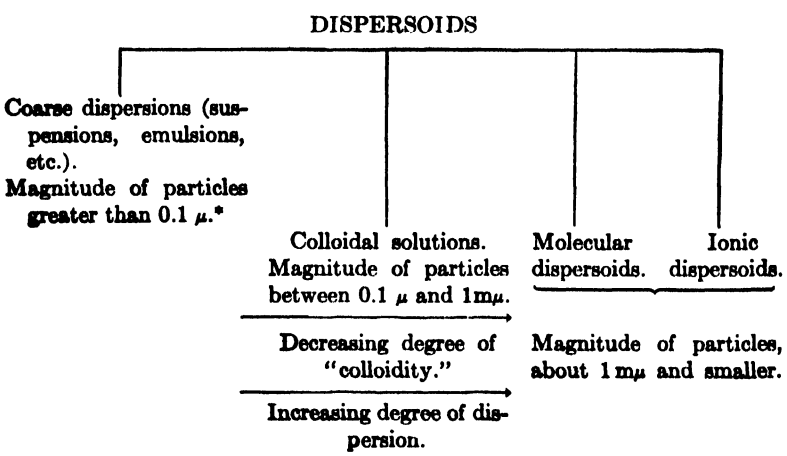
* Jour. Chem. Soc., 61, 148 (1892).

solution of collodion in acetic acid, it is not only possible to separate suspensoids from their dispersion media, but also to effect the concentration of emulsoids. Furthermore, such filters are useful in removing impurities from sols, the impurity passing through the filter in a manner similar to the passage of the solvent through the membrane in the process of dialysis. Ultrafiltration is an exceedingly complex process, involving the phenomena of adsorption and dialysis, in addition to the ordinary process of mechanical separation. The complexity of the process is well illustrated by the phenomena attendant upon the filtration of almost any positive hydrosol. Thus, if we attempt to filter a ferric hydroxide hydrosol through a porous plate, or even through an ordinary filter paper, we shall find that the colloid will be partially retained by the filter. This is due to the fact that the filter becomes negatively charged in contact with water and, on the entrance of the positively-charged sol into the pores of the filter, the colloid is immediately discharged and the disperse phase precipitated. After the pores of the filter become partially stopped with particles of the colloid, the sol will then pass through unchanged.

Classification of Dispersoids. There is abundant evidence in favor of the view, that colloidal solutions and simple suspensions are closely related. Suspensions of all grades exist, from those in which the suspended particles are coarse-grained and visible to the naked eye, down to those in which a high-power microscope is required to render the suspended particles visible. Colloidal solutions have also been shown to be non-homogeneous, the presence of discrete particles being revealed by means of the ultramicroscope. It follows, therefore, that the size of the particles in solution determines whether a substance is to be considered as a colloid or not. At one extreme, we have true solutions in which no lack of homogeneity can be detected, even by the ultramicroscope, and at the other extreme, we have coarse-grained suspensions, in which the particles are visible to the naked eye. Between these two limits all possible degrees of subdivision are possible, and it is a very difficult matter to draw sharp lines of distinction between true solutions and colloidal solutions, on the one hand, and between colloidal solutions and suspensions, on the other.

One of the most satisfactory schemes of classification is that

of von Weimarn and Wo. Ostwald.* Because of the fact that suspensions, colloidal solutions, and true solutions represent varying degrees of dispersion of the solute, all three types of systems are termed by these authors, dispersoids. The dispersoids are classified as shown in the accompanying diagram.



* 1 μ = 1 micron = 0.001 mm.

The Brownian Movement. If a liquid in which fine particles of matter are suspended, such as an aqueous suspension of gamboge, be examined under the microscope, the suspended particles will be seen to be in a state of ceaseless, erratic motion. This phenomenon, which had frequently been observed, was first correctly interpreted, in 1827, by the English botanist, Robert Brown, while examining a suspension of pollen grains. It is commonly known as the *Brownian movement.*

Ever since its discovery, the Brownian movement has been the subject of numerous investigations. It was not until 1863, however, that Wiener suggested that the cause of the phenomenon was the actual bombardment of the suspended particles by the molecules of the suspending medium. Twenty-five years later, a similar conclusion was reached independently by Gouy, who showed that neither light, nor convection currents within the liquid, could possibly give rise to the motion. Furthermore, Gouy showed the movement to be independent of external vibration, and only

* Koll. Zeitschrift, 3, 26 (1908).

slightly influenced by the nature of the suspended particles. The smaller the particles and the less viscous the suspending medium, the more rapid the motion was found to be. By far the most striking feature of the phenomenon, however, is the fact that the motion is ceaseless.

In 1909, Perrin undertook the study of sedimentation equilibrium, which he inferred must be dependent upon the Brownian movement. The results of his investigation are here briefly summarized.

Perrin's Experiments. The first quantitative investigation of the Brownian movement was undertaken by Svedberg in 1906. It has been shown (p. 51), that the mean kinetic energy, E_k, of one mol of a perfect gas is given by the expression,

$$E_k = \tfrac{3}{2}\, pv. \tag{1}$$

Since $pv = RT$, we may write

$$E_k = \frac{3\,RT}{2\,N}, \tag{2}$$

where N denotes the Avogadro Constant, that is, the number of molecules contained in one mol of any gas. It is evident that if E_k can be measured, equation (2) affords a means of calculating N, provided we are warranted in applying an equation which has been derived for the gaseous state, to a suspension of fine particles in a liquid medium. It has already been shown, that the simple gas laws hold for dilute solutions, and therefore, we may assume that, at the same temperature, the mean kinetic energy of the dissolved molecules is equal to that of the gaseous molecules. In other words, at the same temperature, the mean kinetic energy of the molecules of all fluids is the same, and is directly proportional to the absolute temperature. Since the gas laws apply equally well to dilute solutions, containing either large or small molecules, Perrin held that there was no *à priori* reason for assuming that the grains of a suspension should not conform to the same laws. If this assumption be correct, the grains of a uniform suspension should so distribute themselves under the influence of gravity that, when equilibrium is attained, the lower layers will have a higher concentration than the upper layers. In other words, the distribution should be strictly analogous to the distribution of the

air over the surface of the earth, the density being greatest at the surface and diminishing as the altitude increases.

Let us imagine a suspension to be confined within a tall vertical cylinder whose cross-sectional area is s sq. cm. Assuming that the suspension has come to equilibrium under the influence of gravitation, let n be the number of grains per unit of volume, at a height h from the base of the cylinder. Since the concentration diminishes as the height increases, the number of grains at a height, $h + dh$, will be $n - dn$. The osmotic pressure of the grains at the height h, will be $\frac{2}{3} nE_k$, where E_k is the mean kinetic energy of each grain. In like manner, the osmotic pressure at the height, $h + dh$, will be $\frac{2}{3} (n - dn)E_k$. The difference in osmotic pressure between the two levels is $-\frac{2}{3} dnE_k$ and, since the pressure acts over a surface of s sq. cm., the difference of osmotic forces acting over the cross-sectional area of the cylinder is $-\frac{2}{3} s\, dnE_k$. Since the system is in equilibrium, this difference in osmotic forces must be balanced by the difference in the attraction of gravitation at the two levels. Let ϕ be the volume of a single grain, D its density, and δ the density of the suspending medium. The resultant downward pull upon a single grain will be $\phi (D - \delta)g$, where g is the acceleration due to gravity. The volume of liquid between the two levels being sdh, it follows that the total downward pull upon all the grains included between the two levels must be $nsdh\phi (D - \delta)g$. It is this force which opposes the tendency of the grains to distribute themselves uniformly throughout the entire volume of the suspending medium, or, in other words, it is the force which acts in opposition to the osmotic force, $-\frac{2}{3} s\, dnE_k$. When equilibrium is established, these two forces must be equal, and we may then write

$$-\tfrac{2}{3} s\, dnE_k = nsdh\phi (D - \delta)g. \qquad (3)$$

If n_0 and n denote the number of grains per unit of volume at each of two planes, h units apart, we obtain, on integrating equation (3),

$$\tfrac{2}{3} E_k \ln n_0/n = \phi (D - \delta)gh. \qquad (4)$$

On substituting in equation (4), the value of E_k in equation (2), and transforming to Briggsian logarithms, we have

$$2.303\, RT/N \log n_0/n = \tfrac{4}{3} \pi r^3 g(D - \delta)h, \qquad (5)$$

ϕ being expressed in terms of the mean radius, r, of a single grain. It is evident that if we can measure n, n_0, D, and r in equation

(5), the calculation of the Avogadro Constant, N, becomes possible.*

The determination of the density of the grains, D, was carried out in two different ways with suspensions of gamboge and mastic which had been rendered uniform by a process of fractional centrifuging. In the first method, the grains were dried to constant weight at 110°, and then by heating to a higher temperature, a viscous liquid was obtained which, on cooling, formed a glassy solid. The density of this solid was determined by suspending it in a solution of potassium bromide of known density.

In the second method for the determination of D, Perrin measured the masses, m_1 and m_2, of equal volumes of water and suspension, respectively. On evaporating the suspension to dryness, the mass, m_3, of suspended solid contained in m_2 grams of suspension was obtained. If the density of water is d, the volume of the suspended grains will be

$$V = \frac{m_1}{d} - \frac{m_2 - m_3}{d}, \tag{6}$$

and consequently, the density of the grains will be m_3/V. The values of D, obtained by these two methods, were found to be in excellent agreement.

A microscope, furnished with suitable micrometers, was employed in the determination of n and n_0. With the high magnification employed, the depth of the field of view was limited: in fact, the measurements were carried out with a microscope-slide similar to those used for counting the corpuscles in the blood. By focusing the microscope at different depths, the average number of grains in the field of view, at each level, could be counted. Perrin was able to photograph the larger grains at different levels, whereas, with the smaller grains, it was necessary to reduce the field so that relatively few grains were visible. The average number of grains counted at any two different levels would of course give the desired ratio, n_0/n.

The only other quantity in equation (5) to be measured is the average radius of the grains, r. To determine this quantity, Perrin made use of a method similar to that used by Thomson for

* It has been pointed out by Burton, that Perrin, in the derivation of his equation for the distribution of the suspended particles under gravity, failed to take into consideration the fact that they are electrically charged.

counting the number of electrically charged particles in an ionized gas. Stokes has shown that the force required to impart a uniform velocity v, to a particle of radius r, moving through a liquid medium whose viscosity is η, is given by the formula, $6\pi\eta rv$. If the motion be due to gravity, as in the case of suspensions of fine particles, obviously the foregoing expression must be equal to the right-hand side of equation (5), or

$$6\pi\eta rv = \tfrac{4}{3}\pi r^3(D - \delta)g. \qquad (7)$$

From this equation, the value of r can be calculated. The rate at which the grains settled under the influence of gravity was determined by placing a portion of the uniform suspension in a capillary tube, and observing the rate at which the suspension cleared, care being taken to keep the temperature constant.

In order to test the validity of Stokes' law under these conditions, the following modification of the method for the determination of r was introduced. It had been observed that when a suspension is rendered slightly acid, the grains, on coming in contact with the walls of the containing vessel, adhered, while the motion of the grains throughout the bulk of the liquid remained unaltered. In this way it was possible gradually to remove all of the grains from the suspension and count them, and knowing the total volume of suspension taken, the average number of grains per cubic centimeter could be calculated. If the total mass of suspended matter is known, it is an easy matter to calculate the volume of each grain, and from this to compute the radius, r. The value of r, determined in this way, was found to agree with that calculated by the first method, thus proving the validity of Stokes' law when applied to colloidal suspensions. The success with which the entire kinetic theory of the Brownian Movement has been confirmed may be regarded as good evidence for the validity of Stokes' law when applied to colloidal particles.

Five series of experiments carried out by Perrin with gamboge suspensions in which several thousand individual grains were counted, gave as a mean value of N, in equation (5), 69×10^{22}. Similar experiments with mastic suspensions gave $N = 70.0 \times 10^{22}$. These values, it will be found, are in close agreement with the values of Avogadro's Constant given on page 24.*

* In this connection the student should refer to a paper by Westgren. Zeit. phys. Chem., 89, 63 (1914).

The Law of Molecular Displacement. The actual movements of the individual grains of a suspension when observed under the microscope are seen to be exceedingly complex and erratic. The horizontal projections of the paths of three different grains in a suspension of mastic are shown in Fig. 94, the dots representing the successive positions occupied by the particles after intervals of 30 seconds. The straight line joining the initial and final positions of a particle is called the *horizontal displacement* X, of the particle.

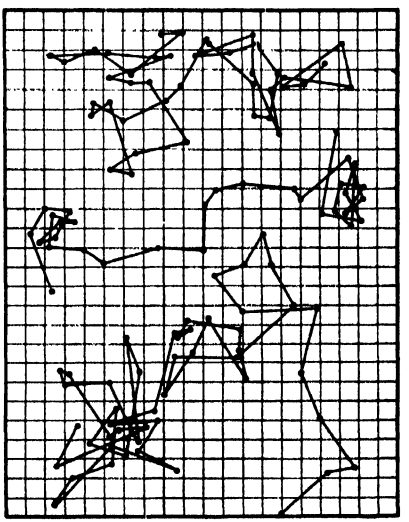


Fig. 94

If the time taken by the particle to move from its initial to its final position be t, Einstein* has shown that the mean value of the square of the X component of the horizontal displacement of a spherical particle of radius r, ought to be

$$X^2 = \frac{RT}{N}\frac{t}{3\pi r\eta}, \qquad (8)$$

where η is the viscosity of the suspending medium, and where the other symbols have their usual significance.

This equation was tested by Perrin, using suspensions of gamboge and mastic. Some of the results obtained are given in the following table: —

VALUES OF N CALCULATED BY EINSTEIN'S EQUATION

Suspension.	r in microns.†	$m \times 10^{15}$.	No. of displacements.	$N \times 10^{-n}$.
Gamboge in water	0.367	246	1500	69
Gamboge in 10% solution of glycerine	0.385	290	100	64
Mastic in water	0.52	650	1000	73
Mastic in 27% solution of urea	5.50	750,000	100	78

† The micron is one-millionth of a meter or one ten-thousandth of a centimeter.

* Zeit. Elektrochem., 14, 235 (1908).

It will be seen, that notwithstanding the large variations in the granular masses of the different suspensions recorded in the table, the values of N, calculated by means of Einstein's equation, are quite concordant. Perrin gives as the mean value of all of his experiments, $N = 68.5 \times 10^{22}$.

Recent Investigations of the Brownian Movement. Nordlund* has recently repeated Perrin's experiments, employing a colloidal solution of mercury, and an arrangement of apparatus, whereby the movements of the particles could be recorded photographically. The mean value of N, derived from twelve carefully executed experiments was, 59×10^{22}, the average deviation of the results of the individual experiments from the mean being approximately 10 per cent.

The Brownian movement in gases has been studied by Millikan,† and also by Fletcher,‡ employing a minute drop of oil as the suspended particle. In the gaseous state, where the intermolecular distances are greater than in the liquid state, not only are the collisions less frequent, but the mean free paths are appreciably longer. These conditions are favorable to the study of the Brownian movement, and offer an opportunity for the determination of the Avogadro Constant with a high degree of accuracy. As the mean of nearly six thousand measurements, Fletcher gives $N = 60.3 \times 10^{22}$, this value being accurate to within 1.2 per cent.

Density of Colloidal Solutions. As we have seen, lyophobe sols are commonly regarded as sols in which the disperse phase is solid, while lyophile sols are considered to be sols in which the disperse phase is liquid. While this distinction between the two classes of sols is generally well defined, it should be borne in mind that there are colloidal solutions in which it is extremely difficult to determine the physical state of the disperse phase.

The fundamental difference between lyophobe and lyophile sols manifests itself most clearly in those properties which undergo appreciable change in consequence of solution. Among these may be mentioned density, viscosity and surface tension.

It was shown by Linder and Picton,§ that the density of lyophobe sols follows the law of mixtures. This is clearly shown by the following table, in which are given the observed and calculated values of the density of a series of arsenious sulphide sols.

* Zeit. phys. Chem., 87, 60 (1914).
† Phys. Rev., 1, 220 (1913).
‡ Ibid., 4, 453 (1914).
§ Jour. Chem. Soc., 67, 71 (1895).

DENSITY OF ARSENIOUS SULPHIDE SOLS

As_2S_3 (grams per liter).	Density (obs.).	Density (calc.).
44	1.033810	1.033810
22	1.016880	1.016905
11	1.008435	1.008440
2.45	1.002110	1.002100
0.1719	1.000137	1.000134

The density of lyophile sols, on the other hand, cannot be calculated from the composition of the sol. This fact may be taken as evidence in favor of the view that a closer relation exists between the disperse phase and the dispersion medium in lyophile than in lyophobe sols.

Viscosity of Colloidal Solutions. Owing to the fact that the concentrations of most lyophobe sols are relatively small, it follows that their viscosities differ but little from the viscosity of the pure dispersion medium. In general, it may be said that the viscosity of lyophobe sols is slightly greater than that of the dispersion medium.

On the other hand, the viscosity of lyophile sols is frequently much greater than that of the pure dispersion medium. The viscosity of lyophile sols also increases with increasing concentration, as is shown by the data of the following table.

VISCOSITY OF LYOPHILE SOLS

Sol.	Temp. 20° Concentration.	Viscosity.
Gelatine.....	1	0.021
Gelatine.....	2	0.037
Silicic acid ...	0.81	0.012
Silicic acid ...	0.99	0.016
Silicic acid ...	1.96	0.032
Silicic acid ...	3.67	0.165

Surface Tension of Colloidal Solutions. The surface tension of lyophobe sols has been shown by Linder and Picton to be practically identical with that of the dispersion medium.

As a general rule, the surface tension of lyophile sols is appreciably smaller than that of the dispersion medium. According to Quincke,* the surface tensions of gelatine sols are appreciably less than the surface tension of the dispersion medium. The difference between lyophobe and lyophile sols, in respect to surface tension, undoubtedly accounts for the fact, that in general, the former are not adsorbed, while the latter are.

Osmotic Pressure of Colloidal Solutions. The osmotic pressure of colloidal solutions is very small. This is what we should expect with solutions of substances which exhibit a slow rate of diffusion. As has been pointed out, diffusion is closely connected with osmotic pressure; hence, if the rate of diffusion is slow, the osmotic pressure exerted by the solution should be small. In some cases, the osmotic pressure is so small as to escape detection. The experimental determination of the osmotic pressure of colloidal solutions is complicated by the difficulty of removing the last traces of electrolytes from the colloid. Owing to their great osmotic activity, the presence of the merest trace of an electrolyte may mask the true osmotic effect of a colloid. It should be borne in mind, however, that semipermeable membranes are much less permeable by colloids than by electrolytes and, in consequence of this fact, the impurities in the colloid would be gradually removed by prolonged dialysis. If the total osmotic pressure were due to the presence of small amounts of impurities in the colloid, then, as these are removed, the pressure should steadily diminish and ultimately become zero. As a matter of fact, the final value of the osmotic pressure of a colloidal solution, although generally very small, is never zero. Of course it must be admitted, that the possibility exists that a minute portion of electrolyte which cannot be removed by dialysis is retained by the colloid, but even then it is difficult to account for the constancy of the final value of the osmotic pressure, irrespective of the method of preparation of the sol. The values of the osmotic pressure of suspensoids are invariably small, and by no means concordant.

The following table gives the results obtained by Duclaux† with colloidal solutions of ferric hydroxide.

Inspection of the table shows that, even in the most concentrated solution, the osmotic pressure is very small. Furthermore,

* Wied. Ann., III, 35, 582 (1885).

† Compt. rend., 140, 1544 (1905); Jour. Chim. Phys., 7, 405 (1909).

it is apparent that, although the osmotic pressure increases with the concentration, the variables are not proportional. Observations on the variation of the osmotic pressure of colloidal solutions with temperature have shown that, in general, as the temperature is raised the pressure increases at a more rapid rate than that required by the law of Gay-Lussac.

OSMOTIC PRESSURE OF COLLOIDAL FERRIC HYDROXIDE SOLS. AT 25°

Concentration, c. Per cent.	(First Series) Pressure, P. Cm. of Water.	P/c.
0.15	0.20	1.4
0.2	0.55	2.7
0.4	2.0	5.0
0.8	7 0	8.7
1.84	22.0	12.0
	(Second Series)	
1.08	0.8	0.7
2.04	2.8	1.4
3.05	5.6	1.8
5.35	12.5	2.3
8.86	22.6	2.5

Employing membranes of collodion and parchment paper, Lillie,* and others, have demonstrated that the values of the osmotic pressure of lyophile sols are, in general, considerably greater than the corresponding values obtained with lyophobe sols. The osmotic pressures of several typical lyophile sols are given in the following table.

OSMOTIC PRESSURES OF LYOPHILE SOLS

Sol.	Concentration (grams per liter).	Osmotic Pressure (mm. of mercury).
Egg albumin.....	12.5	20
Gelatine.....	12.5	6
Starch iodide.....	30	15
Dextrin.....	10	165

* Am. Jour. Physiol., 20, 127 (1907).

It will be observed, that the values of the osmotic pressure in the preceding table are appreciably greater than those given for ferric hydroxide hydrosols. This is in agreement with the well-established fact, that lyophile sols diffuse more rapidly than lyophobe sols. It has been observed, that the value of the osmotic pressure of gelatine solutions, at ordinary temperatures, can be increased by maintaining the solutions at a higher temperature for a short time, and then cooling to the initial temperature. After standing for several days at the original temperature, however, the osmotic pressure of the solution returns to its former value. This phenomenon would seem to indicate that the osmotic pressure of colloidal solutions is not completely defined by the two variables, temperature and concentration. It has been suggested, that the degree of aggregation of the colloid is partially dependent upon the temperature, the molecular aggregates tending to break up as the temperature is raised, thus increasing the number of dissolved units and therefore causing a corresponding increase in the osmotic pressure.

Molecular Weight of Colloids. We have already learned, that the knowledge of the osmotic pressure of a solution enables us to calculate the molecular weight of the solute, provided the solution is dilute, and obeys the gas laws. As we have seen, other factors than concentration and temperature determine the osmotic pressure of colloidal solutions, so that we are not justified in attempting to calculate the molecular weight of a colloid from the observed value of the osmotic pressure of its solution. Values for the molecular weight of colloids, calculated from their effect on the vapor pressure, the boiling-point, and the freezing-point of the solvent are also untrustworthy, since the same factors which influence the osmotic pressure, necessarily affect these related properties. This becomes evident when we reflect that an osmotic pressure of 1 mm. of mercury corresponds to a depression of the freezing-point of water about 0°.0001. Owing to the difficulty of obtaining absolutely pure lyophile sols, all determinations of their freezing-point depressions must be affected with an experimental error appreciably larger than the observed depression. Hydrosols of albumin, gelatine, etc., prepared with extreme care by Bruni and Pappada,* failed to produce any detectable depression of the freezing-point of water.

* Rend. R. Accad. dei Lincei. (5), 9, 354 (1900).

Electroendosmosis. The movement of a liquid through a porous diaphragm, due to the passage of an electric current between two electrodes placed on opposite sides of the diaphragm, is known as *electroendosmosis*. This phenomenon, which was first observed by Reuss, in 1807, has since been made the subject of numerous investigations by Wiedemann,* Quincke† and Perrin,‡ the latter having worked out a satisfactory theoretical interpretation of the phenomenon. If a porous partition be placed in the horizontal portion of a U-tube, and an electrode be inserted in each arm of the tube, it will be found, on filling the tube with a feebly conducting liquid, and passing a current, that the liquid will commence to rise in one arm of the tube, and will continue to rise, until a definite equilibrium is established. For a given difference of potential between the two electrodes, there will be a definite difference in the level of the liquid in the two arms of the tube. The majority of substances acquire a negative electric charge when immersed in water. The water, under these conditions, becomes positively charged and will, in consequence, migrate toward the cathode. On the other hand, certain substances acquire a positive charge, on immersion in water, and in these cases the direction of migration will obviously be reversed.

It has been found that acids cause negative diaphragms to become less negative, and positive diaphragms to become more positive. The action of alkalies is, as we should expect, the reverse of that of acids. There is an interesting connection between the valence of the ions, resulting from the dissociation of dissolved salts, and the difference of potential existing between the liquid and the diaphragm. When the diaphragm is positively charged, the difference of potential is found to be conditioned by the valence of the anion, and when the diaphragm is negatively charged, the difference of potential is determined by the valence of the cation.

Cataphoresis. When a difference of potential is established between two electrodes immersed in a suspension of finely-divided quartz, or shellac, the suspended particles move toward the positive electrode. This phenomenon is called *cataphoresis*, and was first observed by Reuss, and later by Linder and Picton.§ They showed that when the terminals of an electric battery are connected

* Pogg. Ann., 87, 321 (1852).
† Ibid., 113, 513 (1861).
‡ Jour. Chim. Phys., 2, 601 (1904).
§ Jour. Chem. Soc., 61, 148 (1892)

to two platinum electrodes dipping into a colloidal solution of arsenious sulphide, there is a gradual migration of the colloid to the positive pole. A similar experiment with a solution of colloidal ferric hydroxide resulted in the transport of the dissolved colloid to the negative pole. It follows, therefore, that the particles of colloidal arsenious sulphide are negatively charged, while those of colloidal ferric hydroxide carry a positive charge. It has been found that most colloids are electrically charged. In the following table some typical colloids are classified according to the character of their electrification in aqueous solution.

ELECTRICAL CHARGES OF HYDROSOLS

Electro-positive.	Electro-negative.
Metallic hydroxides	All the metals
Methyl violet	Metallic sulphides
Methylene blue	Aniline blue
Magdala red	Indigo
Bismarck brown	Eosine
Hæmoglobin	Starch

The nature of the charge varies with the dispersion medium used; colloidal solutions in turpentine, for example, having charges opposite to those in water.

Direct measurements of the velocity with which the particles move in cataphoresis have been made by Cotton and Mouton.* By observing with a microscope the distance over which a single particle traveled in a given interval of time, under a definite potential gradient, they calculated the average velocity of migration of a number of lyophobe sols. The following table gives the velocity of migration of a few typical lyophobe sols.

It will be observed that not only are the velocities of migration nearly constant, but also that they are apparently independent of the size and nature of the particles.

The presence of electrolytes, especially acids and bases, exercises a marked effect upon the electrical behavior of suspensoids. Owing to the comparative instability of suspensoids, the addition of electrolytes usually results in the complete precipitation of the colloid.

* Jour. Chim. Phys., 4, 365 (1906).

VELOCITY OF MIGRATION OF LYOPHOBE SOLS

Suspensoid.	Average Diameter of Particles.	Velocity cm./sec. for Unit Potential Gradient.
Arsenic trisulphide	50 μ	22×10^{-5}
Quartz	1 $m\mu$	30×10^{-5}
Gold (colloidal)	<100 $m\mu$	40×10^{-5}
Platinum (colloidal)	<100 $m\mu$	30×10^{-5}
Silver (colloidal)	<100 $m\mu$	23.6×10^{-5}
Bismuth (colloidal)	<100 $m\mu$	11.0×10^{-5}
Lead (colloidal)	<100 $m\mu$	12.0×10^{-5}
Iron (colloidal)	<100 $m\mu$	19.0×10^{-5}
Ferric hydroxide (colloidal)	100 $m\mu$	30.0×10^{-5}

W. B. Hardy* has found that the direction of migration of albumin, modified by heating to 100° C., is dependent upon the reaction of the dispersion medium. A very small quantity of free base causes the particles of albumin to move toward the positive electrode, while the addition of an equally small amount of acid results in a reversal of the direction of migration. Similar reversals of charge have been observed by Burton† in colloidal solutions of gold and silver. When small amounts of aluminium sulphate are added to colloidal solutions of these metals, the charge is gradually neutralized and, eventually, the colloidal particles acquire a reversed charge.

Electrical Conductance of Colloidal Solutions. The electrical conductance of lyophobe sols differs so slightly from that of the pure dispersion medium, that it is difficult to decide whether the small increase in conductance may not be due to the presence of traces of adsorbed electrolytes. In order to ascertain to what extent the conductance of lyophobe sols is dependent upon the presence of adsorbed electrolytes, Whitney and Blake‡ investigated the effect of successive electrolyses upon the conductance of a gold hydrosol. If the pure sol is incapable of enhancing the conductance of the dispersion medium, then as the sol is subjected to successive electrolyses, the conductance should steadily diminish and, ultimately, become identical with that of the dispersion medium.

* Jour. Physiol., 24, 288 (1899). † Phil. Mag., 12, 472 (1906).
‡ Jour. Am. Chem. Soc., 26, 1339 (1904).

Whitney and Blake found that the conductance converged to a definite limiting value, which was slightly greater than the conductance of the dispersion medium. From these experiments we seem to be warranted in concluding, that lyophobe sols conduct the electric current very feebly.

Lyophile sols appear to conduct rather better than lyophobe sols.* Whitney and Blake measured the conductance of silicic acid and gelatine sols, and found the specific conductance of the former to be 100×10^{-6} reciprocal ohms, and that of the latter to be 68×10^{-6} reciprocal ohms. On the other hand, Pauli† found that an albumin sol, which had been prepared with extreme care, was virtually a non-conductor. It should be remembered, however, that the albumins are closely related to the simple amino-acids, which are known to be exceedingly poor conductors.

Precipitation of Colloids by Electrolytes. One of the most important and interesting divisions of the chemistry of colloids, is that which treats of the precipitation of lyophobe and lyophile sols by electrolytes. Colloidal solutions are more or less unstable systems, irrespective of the methods employed in their preparation, and the addition of a small amount of an electrolyte is frequently found to be sufficient to cause the sol immediately to become opalescent, and ultimately to precipitate, leaving the dispersion medium perfectly clear and free from the disperse phase.

Some exceptions to this general statement as to the behavior of colloids are known. For example, Whitney and Blake‡ found that precipitated gold could be caused to return to the colloidal state by treatment with ammonia, while Linder and Picton§ discovered that a ferric hydroxide hydrosol, which had been precipitated with sodium chloride, could be restored to the colloidal condition by simply removing the electrolyte with water. The sedimentation of suspensions, such as kaolin in water, is also promoted by the addition of electrolytes. On the other hand, the addition of some non-electrolytes frequently causes an increase in the stability of a suspensoid.

Precipitation of Lyophobe Sols. The phenomenon of the precipitation of lyophobe sols has been carefully investigated by

* This may be due to greater difficulties involved in purification.

† Beitrag. Chem. Phys. Path., 7, 531 (1906).

‡ Jour. Am. Chem. Soc., 26, 1341 (1904).

§ Jour. Chem. Soc., 61, 114 (1892); 87, 1924 (1905).

Freundlich.* He has found, that an amount of electrolyte which is incapable of bringing about an instantaneous precipitation, may become effective after an interval of time. He has also shown, that the total quantity of electrolyte required to precipitate a lyophobe sol completely, depends upon whether the electrolyte is added all at one time, or in successive portions.

In order to compare the precipitating action of various electrolytes, Freundlich proposed the following procedure, which prevents the possibility of irregularities due to the time factor:— To 20 cc. of a solution of a lyophobe sol, 2 cc. of the solution of the electrolyte are added, the resulting solution being shaken vigorously; the mixture is then set aside for two hours, after which a small portion is filtered off, and the filtrate is examined for the colloid. In the following table, some of the results obtained by Freundlich with colloidal solutions of ferric hydroxide are given. The data represent the minimum concentration for each electrolyte which produced precipitation in two hours.

PRECIPITATING ACTION OF ELECTROLYTES ON FERRIC HYDROXIDE HYDROSOL
(16 milli-mols $Fe(OH)_3$ per liter)

Electrolyte.	Concentration (milli-mols per liter).	Electrolyte.	Concentration (milli-mols per liter).
NaCl	9.25	HCl	400 ca.
KCl	9.03	$Ba(OH)_2$	0.42
$BaCl_2$	9.64		
KNO_3	11.9	K_2SO_4	0.204
KBr	12.5	$MgSO_4$	0.217
$Ba(NO_3)_2$	14.0	$K_2Cr_2O_7$	0.194
KI	16.2	H_2SO_4	0.5 ca.

It will be seen that very small amounts of the electrolytes are required to precipitate the colloid, and further, that the precipitating power of an electrolyte is dependent upon the charge of the negative ion. The greater the charge, the smaller is the quantity of electrolyte required to produce precipitation.

The significance of the relation between ionic charge and precipitating power was first pointed out by Schulze, and later verified

* Zeit. phys. Chem., 44, 131 (1903).

by Hardy.* The Schulze-Hardy rule may be stated as follows:— *The precipitation of a colloidal solution is determined by that ion of an added electrolyte which has an electric charge opposite in sign to that of the colloidal particles.*

It has already been pointed out, that colloidal particles of arsenious sulphide are negatively charged, hence, according to the Schulze-Hardy rule, the positive ions of the added electrolyte will condition the precipitation of the lyophobe sol. The experiments of Freundlich confirm this prediction, as is shown by the following table:

PRECIPITATING ACTION OF ELECTROLYTES ON ARSENIOUS SULPHIDE HYDROSOL
(7.54 milli-mols As_2S_3 per liter)

Electrolyte.	Concentration (milli-mols per liter).	Electrolyte.	Concentration (milli-mols per liter).
KCl	49.5	$CaCl_2$	0.649
KNO_3	50.0	$SrCl_2$	0.635
$KC_2H_3O_2$	110.0	$BaCl_2$	0.691
NaCl	51.0	$Ba(NO_3)_2$	0.687
LiCl	58.4	$ZnCl_2$	0.685
$MgCl_2$	0.717	$AlCl_3$	0.093
$MgSO_4$	0.810	$Al(NO_3)_3$	0.095

Precipitation and Valence. An examination of the preceding tables reveals the fact, that although the ionic concentration necessary to bring about precipitation, in accordance with the Schulze-Hardy rule, decreases with increasing valence, the diminution in concentration is not, as we might expect, inversely proportional to the valence of the precipitating ion. The absence of any simple quantitative relation between the valence of an ion and its precipitating concentration, is undoubtedly due to the influence of several potent factors, such as adsorption, and the protective action of ions whose electric charge is of the same sign as that of the colloidal substance.

Precipitation of Lyophile Sols. The action of electrolytes on lyophile sols is much more obscure than the action of electrolytes on lyophobe sols. Nothing approaching a generalization similar to

* Jour. fur prakt. Chem., 25, 431 (1882); 27, 320 (1883).

Schulze's law for the precipitation of lyophobe sols has been found to apply to the precipitation phenomena manifested by lyophile sols.

The addition of salts to gelatine generally causes irreversible precipitation, provided the concentration of the salt is not too low. The precipitation of albumin by some salts is reversible, while by others it is irreversible. Those transformations which are initially reversible, gradually become irreversible on standing. Although relatively concentrated solutions of salts of the alkalies and alkaline earths are required to precipitate albumin, very dilute solutions of the salts of the heavy metals are found to be sufficient to bring about complete precipitation.

Action of Heat on Lyophile Sols. When an albumin hydrosol is gradually heated, a temperature is ultimately reached at which coagulation occurs. The exact nature of this transformation is not understood, but it is believed to be largely chemical. This belief is based upon the fact, that the reaction of the natural albumins toward litmus is altered by heating. Slight acidity of the sol is essential to complete coagulation, while an excess or a deficiency of acids causes a portion of the albumin to remain in the sol. The presence of various salts has been found to exert a marked influence on the temperature of coagulation of albumin. The coagulation temperature is invariably raised at first, attaining a constant value in some cases, while in others it decreases, after reaching a maximum temperature.

Gelatine, on the other hand, is not amphoteric, like albumin, but is essentially acid. If a moderately concentrated gelatine sol is prepared with hot water, on cooling it sets to a jelly, which is readily reconverted into a sol on warming. This change does not take place at a definite temperature.

In studying the phenomenon of gelation, either the temperature, or the time of gelation, may be determined. The melting-point of pure gelatine ranges from 26° to 29°, while the solidifying temperature lies between 25° and 18°.* The melting and solidifying temperatures of gelatine sols vary with the concentration; a 5 per cent sol melts at 26°.1 and solidifies at 17°.8, while a 15 per cent sol melts at 29°.4 and solidifies at 25°.5.† The temperature of the

* See Sheppard & Sweet. Jour. Ind. and Eng. Chem., 13, 423 (1921).

† These are not melting and freezing points in the strict sense of the definition of those terms, implying a condition of equilibrium between solid and liquid phases.

gel-sol transformation is affected by the addition of salts, some tending to raise the temperature of gelation, and others to lower it.

It is noteworthy, that the influence of salts on the temperature of gelation of agar-agar, and other similar substances, is analogous to their effect on gelatine, the same lyotropic sequence being maintained.

Protective Colloids. The precipitating action of electrolytes on lyophobe sols may be inhibited by adding to the solution of a lyophobe sol, a reversible colloid. The protective action of a reversible colloid is not due, as might be supposed, to the increased viscosity of the medium and the resultant resistance to sedimentation, since amounts of a reversible colloid, too minute to produce any appreciable increase in the viscosity of the medium, can prevent precipitation. Thus, Bechhold* has shown, that while a mixture of 1 cc. of a suspension of mastic and 1 cc. of a 0.1 molar solution of $MgSO_4$, diluted to 3 cc. with water, is completely precipitated in 15 minutes, no precipitation will occur within 24 hours, if two drops of a 1 per cent solution of gelatine be added, before diluting to 3 cc. Gum arabic and ox-blood serum exert a similar protective action when added to a suspension of mastic.

The protective power of reversible colloids differs widely, and Zsigmondy† has attempted to make this the basis of a method of classification of colloidal substances. A red colloidal gold sol becomes blue on the addition of a small amount of sodium chloride, owing to the increase in the size of the colloidal particles. Various colloidal substances when added to a red colored gold sol protect the colloidal particles from precipitation by a solution of sodium chloride, no change in color following the addition of the electrolyte. A definite amount of each colloidal substance is required to prevent the change, from red to blue, in the color of the gold sol. In employing this color change as a means of differentiating colloidal substances, Zsigmondy introduced the so-called "gold number." This may be defined as the weight in milligrams of a colloidal substance which is just insufficient to prevent the change from red to blue in 10 cc. of a gold sol, after the addition of 1 cc. of a 10 per cent solution of sodium chloride. The following table gives the gold numbers of a few colloids.

* Zeit. phys. Chem., 48, 408 (1904).

† Zeit. analyt. Chem., 40, 697 (1901).

GOLD NUMBERS OF COLLOIDS

Colloid.	Gold Number.
Gelatine	0.005–0.01*
Casein (in ammonia)	0.01
Egg-albumin	0.15–0.25
Gum arabic	0.15–0.25; 0.5–4
Dextrin	6–12; 10–20
Starch, wheat	4–6 (about)
Starch, potato	25 (about).
Sodium stearate	10 (at 60°); 0.01 (at 100°)
Sodium oleate	0.4–1
Cane sugar	8
Urea	8

* See Elliott and Sheppard. Jour. Ind. and Eng. Chem. 13, 699 (1921).

The gold number has proven useful in differentiating the various kinds of albumin, as is shown in the following table.

GOLD NUMBERS OF ALBUMINS

Albumin.	Gold Number.
Egg white (fresh)	0.08
Globulin	0.02–0.05
Ovomucoid	0.04–0.08
Albumin (Merck)	0.1–0.3
Albumin (cryst.)	2–8
Albumin (alkaline)	0.006–0.04

The addition of alkali to any one of the first five albumins of the above table reduces the gold number to that of alkaline albumin. Sulphide sols may be protected as well as metallic sols, and furthermore, the ability to exert protective action is not confined to organic colloids alone.

In general, it may be said that when a lyophobe sol is mixed with a lyophile sol in the proper proportions, the lyophobe sol acquires most of the characteristic properties of the protecting colloid. The masking of the properties of a lyophobe sol by a protecting colloid, is probably to be ascribed to the formation of a thin film of adsorbed lyophile colloid over the lyophobe colloid.

Mutual Precipitation. A further deduction from the electrical theory of precipitation is, that when two oppositely-charged colloids are mixed, they should precipitate each other, and the resulting precipitate should contain both colloids. Experiments carried out by Biltz* have confirmed these predictions. He showed that when a solution of a positively-charged colloid is added to a solution of a negatively-charged colloid, precipitation occurs, unless the quantity of the added colloid is either relatively very large, or very small. Just as the amount of precipitation caused by the addition of an electrolyte to a sol is conditioned by the rate at which the electrolyte is added, so also the precipitation of one colloid by another is dependent upon the manner in which the two sols are mixed. The extent to which one sol is precipitated by another sol of opposite sign, is largely determined by the amount of the one that is added to a definite amount of the other. This is clearly shown by the following table, which gives the results obtained by Biltz, on adding ferric hydroxide sol to 2 cc. of an antimony trisulphide sol containing 2.8 mg. per cc.

PRECIPITATION OF COLLOIDAL ANTIMONY TRISULPHIDE BY COLLOIDAL FERRIC HYDROXIDE

Fe_2O_3(mg.).	Immediate Result.	Result After One Hour.
0.8	Cloudy	Almost homogeneous
3.2	Small flakes	Unchanged
4.8	Flakes	Yellow liquid
6.4	Complete precipitation	Complete precipitation
8.0	Slow precipitation	Complete precipitation
12.8	Cloudy	Slight precipitation
20.8	Cloudy	Homogeneous

It will be seen, that the addition of a small amount of ferric hydroxide produces hardly any precipitation. With the addition of larger amounts of ferric hydroxide, the amount of precipitation increases, until finally, complete precipitation is attained. The addition of larger quantities of ferric hydroxide produces either little, or no, precipitation. It has been found, that at the concentration which just produces complete precipitation, the electrical charges of the two sols are equivalent. When the amount of

* Berichte, 37, 1095 (1904).

ferric hydroxide exceeds that required for complete precipitation, it is more than probable that the particles of colloidal antimony trisulphide are completely enveloped by the particles of ferric hydroxide, and thereby rendered inactive.

When we come to study the action of one lyophile sol on another, we find, as might be expected from the general behavior of lyophile sols toward electrolytes, that the phenomena are more complex, and very much less well-defined, than with lyophobe sols. Although mutual precipitation does take place with lyophile sols, the close resemblance between lyophile sols and true solutions renders the phenomenon more or less indistinct.

When a lyophobe sol is added to a lyophile sol having an opposite electric charge, precipitation may, or may not, occur, according to the relative amounts of the two colloids in the mixture. When the two colloids are present in electrically equivalent quantities, either precipitation will occur, or one colloid will exert a protective action on the other.

Polar and Nonpolar Compounds. Early in the development of the molecular theory, the idea was advanced that the center of the field of molecular attractive and repulsive forces is not necessarily coincident with the center of mass of the molecule, but is more often than not shifted toward one of the atoms, or groups of atoms, of which the molecule is composed. Thus, the oxygen atom has long been regarded as one whose field of force is only partially neutralized by the fields of force of the contiguous atoms with which it is in chemical combination. In a compound such as formic acid, H.COOH, there evidently exists a strong field of force which manifests itself in the high surface tension and high critical temperature of the acid. In the hydrocarbon ethane, C_2H_6, however, the molecules exert relatively small attraction for one another, as is evidenced by the order of magnitude of its physical constants. It follows, therefore, in a compound such as propionic acid, C_2H_5.COOH, in which the molecule may be regarded as made up of a nonpolar molecule of ethane in combination with a polar molecule of formic acid, that the resulting compound will be polar with its field of force concentrated in the neighborhood of the carboxyl group.

Since, according to the modern theory of atomic structure, the atom is considered as made up of a positively charged nucleus with an attendant system of electrons as satellites, it follows

that the molecule may be represented as a system of positive nuclei and electrons, the relative positions of whose centers of mass can be estimated from the spatial arrangement of the atoms in the molecule. In terms of this theory, a molecule will be polar when the distance between the centers of mass is relatively large. The molecule is to be thought of as an electrical doublet having the total positive charge concentrated at one center of mass and the total negative charge at the other. Of course in the case of complex molecules made up of long chains of atoms, it is often necessary to consider the electrification as distributed amongst several centers.

Molecular Orientation. Owing to the lack of uniformity in the distribution of their electric charges, polar molecules tend to orient themselves in such a manner as to reduce their potential energy to a minimum. The subject of molecular orientation has been investigated by Langmuir,* and also by Harkins.† Langmuir showed that the area of a surface of water over which a fatty acid can spread is independent of the length of its chain of carbon atoms. This suggests that the molecules of the acid must be oriented with the hydrocarbon portion of the molecules lying in the surface of the liquid and the carboxyl groups directed inwards towards the main body of the liquid. He extended this theory to include all polar molecules, stating that orientation will always take place in such a direction as to reduce the potential energy to a minimum. Thus, if the greater part of the force of mutual attraction is concentrated at one end of a molecule, the molecule will orient itself in such a direction that the polar end is nearest to the main body of the liquid.

Practically the same views were advanced independently by Harkins, who has adduced a wealth of experimental evidence in support of the theory.†

Emulsions. A dispersion of minute drops of one liquid in another is known as an *emulsion*. If an emulsion contains relatively little of the disperse phase, its properties resemble those of the lyophobe sols. That is, the disperse phase exhibits the Brownian movement, is precipitated by electrolytes, and can even be separated from the dispersion medium by the process of ultrafiltration.

Two liquids which are mutually insoluble may be emulsified

* Langmuir, Jour. Am. Chem. Soc., **39**, 1848 (1917).

† Harkins, Ibid., **39**, 354, 541 (1917).

by prolonged mechanical agitation, but if the resulting emulsion contains much more than one per cent of the disperse phase, it is unstable, and the component liquids soon separate into two layers. For example, a small portion of benzene in a large volume of water may be emulsified by shaking, but on standing, the minute droplets of benzene soon coalesce and the liquids separate into two layers. The larger the proportion of benzene in the mixture, the more unstable the emulsion becomes.

While stable emulsions of two pure liquids cannot be prepared, they may readily be stabilized by the addition of a third substance known as an *emulsifying agent*, or *emulsifier*. Thus, if a small amount of sodium oleate be dissolved in water and this solution be vigorously shaken with benzene, a stable emulsion will result. Emulsions of kerosene in water, containing as high as 99 per cent of oil in a 1 per cent soap solution, have been prepared and studied by Pickering. The emulsion containing 99 per cent of kerosene was found to resemble a solid, and had the consistency of blanc mange. It frequently happens that a small amount of unsuspected impurity functions as an emulsifying agent.

Two main types of emulsion are recognized — (1) emulsions in which oil is dispersed in water, known as the *oil-water* type, and (2) emulsions in which water is dispersed in oil, known as the *water-oil* type. The word "oil" is here used to designate any liquid which is insoluble in water. Of these two types of emulsion, the first is by far the more common.

While the alkali soaps are excellent emulsifying agents for emulsions of the first type, it has been found that they are not satisfactory for emulsions of the second type. On the other hand, while the soaps of the heavy metals are not good emulsifying agents for emulsions of the first type, they are found to be most effective for those of the second type. Gum arabic, gelatin, agar-agar, albumin, and all of the so-called "solvated colloids" are also good emulsifying agents.

Although it is often difficult to decide from a superficial examination whether an emulsion is of the oil-water or water-oil type, the question may be definitely answered by placing a few drops of the emulsion under the microscope and stirring in successively a little of one phase, and then a little of the other. While the external phase will readily mix with the emulsion, the internal phase will not.

The preparation of stable emulsions is of great practical importance in pharmacy as well as in cookery and in the arts. The reverse process of breaking up emulsions, known as "de-emulsification," is also of considerable practical importance. For example, petroleum frequently contains large amounts of emulsified water which it is very desirable to remove. Several methods are available for de-emulsification; among these may be mentioned the Cottrell process, employing high tension electric current, and methods based upon filtration, freezing out and centrifugal separation.

Theories of Emulsification. Numerous theories have been advanced in explanation of the phenomena of emulsification. Thus, it was believed by Plateau and Quincke that the important function of the emulsifying agent is its power to lower the interfacial tension between the two liquids forming the emulsion. The alkali soaps which have been mentioned as among the best known emulsifying agents are known to produce marked lowering in the surface tension of water. For example, in an emulsion of benzene and water, the interfacial tension is approximately 35 dynes per cm., but when enough sodium oleate is dissolved in the water to make the solution 0.01 molal, the interfacial tension is reduced to about 2 dynes per cm.

According to another theory, emulsifying power is ascribed to the tendency of the emulsifying agent to form hydrates and, thus, bind to itself the molecules of the aqueous phase.

Bancroft* holds that the type of emulsion is determined by the phase which is the best solvent for the emulsifying agent. He maintains that, "If the adsorption of the emulsifying agent lowers the surface tension on the water side of the interface more than it does on the oil side, the interface will tend to curve so as to be convex on the water side, and we shall have a tendency to emulsify oil in water. If the adsorption of the emulsifying agent lowers the surface tension on the oil side of the interface more than it does on the water side, the interface will tend to curve so as to be concave on the water side, and we shall have a tendency to emulsify water in oil. The simplest way, then, to emulsify oil in water is to add a water-soluble colloid which is adsorbed strongly at the interface, and the simplest way to emulsify water in oil is to add an oil-soluble colloid which is adsorbed strongly in the interface."

* Bancroft, "Applied Colloid Chemistry," p. 261.

It has been shown by Bhatnagar* that all emulsifying agents having an excess of negative ions adsorbed on them, and wetted by water, yield oil-in-water emulsions, while emulsifying agents having an excess of adsorbed positive ions, and wetted by oil, yield water-in-oil emulsions.

According to Langmuir†, and Harkins‡, the most effective emulsifying agents are those whose molecules consist of long chains of carbon atoms with a strong polar group, such as the carboxyl group, at one end. The nonpolar end of the molecule is assumed to direct itself towards the oily liquid, while the polar end tends to enter the aqueous phase. If the nonpolar ends of the molecules can pack together more closely than the polar ends, the interfacial film will be bent towards the oil, and an emulsion of oil in water will result. This is commonly known as the oriented wedge theory of emulsification. The theory has been more fully developed by Hildebrand,§ who has endeavored to show how it may be applied to the behavior of all emulsifying agents for which the necessary data are available. Stamm and Kraemer,|| however, have recently claimed that much of the original evidence for the oriented wedge theory of emulsions cannot be substantiated and that predictions based upon the theory have not been realized.

Gels and Gelatinous Precipitates. When the conditions within a solution are so modified as to depress the solubility of the solute below a certain definite value, precipitation invariably occurs. The precipitate may be either crystalline, or amorphous, in character. When the precipitate retains an appreciable quantity of the liquid in which it was dissolved, in the form of a semi-solid mass, it is termed a "gelatinous" precipitate, whereas if all of the liquid is initially retained, the precipitate is known as a "jelly" or "gel." A gel not only possesses greater rigidity and is more elastic than a gelatinous precipitate, but also it has a more uniform structure. On standing, gels frequently undergo an appreciable shrinkage in volume with a simultaneous extrusion of liquid; the latter phenomenon is termed *syneresis*. Gelatinous precipitates

* Bhatnagar, Jour. Chem. Soc., 119, 61, 1760 (1921).

† Langmuir, Chem. Met. Eng., 15, 468 (1916); Jour. Am. Chem. Soc., 39, 1848 (1917).

‡ Harkins, Davies and Clark, Jour. Am. Chem. Soc., 39, 354, 541 (1917).

§ Finkle, Draper and Hildebrand, Ibid., 45, 2780 (1923).

|| Stamm and Kraemer, Jour. Phys. Chem., 30, 992 (1926).

settle quite rapidly and are more or less opaque, while gels require an appreciable time to develop, and are either translucent, or transparent. There is, however, no sharp line of demarcation between a gelatinous precipitate and a jelly, and because of this fact, some authorities use the term " gel " to include both.

Gel Formation. Gels may be formed by several different methods; these will be briefly considered in the succeeding paragraphs.

(*a*) *Gel Formation by Cooling.* The production of gels by the cooling of a sol is one of the simplest and most familiar methods. As an example of this method, we may cite the formation of a typical gel by cooling to room temperature a 2 per cent gelatin sol in hot water. The resulting gel will be found to be both stiff and transparent. It seems probable that when such a sol cools, the molecular aggregates unite to form long filaments which interlace and give rise to a structure resembling a heap of brush-wood. Such a structure would account for the entangling of a large volume of water in the capillary spaces. It is highly probable, however, in gels with well-developed structure, that the aggregates of the gel forming substance are hydrated by the adsorption of water, with a consequent thickening of the filaments. In such a gel, the water which is not actually adsorbed is probably held by capillary attraction.

It is important to distinguish between " true " and " false " gels. To the first group belong gels of the gelatin, agar, or soap type, in which interlacing fibers have not been definitely proven to exist. To the second group are assigned all magmas of interlacing, needle-like crystals which are capable of entangling large volumes of water without actually adsorbing it on the crystal faces. An example of a false gel is afforded by caffeine; if 5 grams of this substance be dissolved in 100 cc. of boiling water, and the solution set aside to cool over night, the beaker containing the crystal network may be inverted without loss of water. A close examination reveals a structure composed of comparatively fine crystalline needles from which the greater part of the water can be removed by stirring or pressing. Between true and false gels as extremes, a wide gradation of gels is found to exist.

The solubility of the liquid in the solid, and the length and fineness of the crystals, or filaments, constitute the dominant factors controlling gel structure.

(*b*) *Gel Formation by Metathesis.* This common method of gel formation may be illustrated by the addition of an acid to a solution of sodium silicate in suitable concentrations. Application of the methods of X-ray analysis to silicic acid gels has failed to reveal any indication of the existence of crystalline structure until the gel has commenced to dry. Although reaction between an acid and a silicate solution proceeds rapidly, it is possible, by proper regulation of the concentrations of the solutions, to delay the completion of gel formation for fully a month. This retardation of the setting of a silicic acid gel is attributed either to the slowness with which complete hydration is accomplished in the presence of certain ions, or to the formation of chains of silica molecules analogous to the carbon chains in organic compounds. If the silica molecules develop into polysilicic acids, a filamentous structure possessing marked adsorbing power would result. It has been shown by Lenher* that when silicic acid gels are subjected to a pressure of 300 tons per sq. in., practically all of the adsorbed water could be expressed, and from the amount of water so obtained he computed that practically one molecule of water was present for every two molecules of silicic acid in the gel.

(*c*) *Gel Formation by a Coagulating Liquid.* When chloroform is added to a nitrocellulose sol in amyl acetate, coagulation occurs and a transparent, viscous gel is obtained. It is of interest to note that when the gel is pressed between the fingers, it is possible to remove nearly all of the liquid, leaving a mass of moist cotton fiber in the hand. Apparently, the greater part of the liquid was retained by the capillary action of the fibers.

(*d*) *Gel Formation by Coagulating Ions.* In many instances the dispersed particles of a sol are prevented from coagulating to form gels because of the repellent action of adsorbed ions. This result will follow whether we have adsorbed negative ions in a negative sol, or adsorbed positive ions in a positive sol. If to such a sol an excess of oppositely charged ions be added, the charge due to the adsorbed ions will be neutralized and opportunity afforded for coagulation.

In this manner, Weiser† prepared a green gel of hydrous chromic oxide containing 85 liters of water to one mol of chromic oxide. To a positive sol of hydrous chromic oxide he added just

* Lenher, Jour. Am. Chem. Soc., **43**, 391 (1921).

† Weiser, Jour. Phys. Chem., **26**, 430 (1922).

sufficient potassium chromate to bring about coagulation within a couple of hours. The effective coagulating agent in this case was the divalent negative ion, CrO_4''. It was found that the addition of too little chromate caused incomplete precipitation, whereas the addition of an excess gave rise to a gelatinous precipitate only.

(*e*) *Gel Formation by Dialysis.* Gel formation may be inhibited by the presence in a colloidal solution of ions which tend to peptize, or redisperse, the solid phase. If such a colloidal solution is subjected to dialysis, the peptizing ions will be gradually removed and conditions favorable to gel formation established. For example, Grimaux* observed that when precipitated ferric arsenate was peptized by ferric chloride, and the resulting sol subjected to dialysis, a clear red gel was obtained.

Emulsion Gels. In a preceding section of this chapter it was pointed out that in an emulsion the emulsifying agent is concentrated at the interface between the disperse and continuous phases. It can be shown that if the disperse phase is in the form of spherical close packed drops, like oranges in a box, their combined volume will represent about 74 per cent of the total volume. Obviously when the aggregate volume of the disperse phase exceeds that corresponding to close packing, a flattening of the drops must occur and, in consequence, a honeycomb structure will gradually develop. Thus, a 75 per cent emulsion of kerosene in water, to which 0.4 per cent of gelatin has been added as an emulsifying agent, forms a gel of such rigidity that scarcely any evidence of flow is observed when a tube containing the emulsion is inverted.

Special Gels. While numerous examples of different types of gels might be given, in the limited space at our disposal we must confine ourselves to a brief description of three gels of special interest.

A remarkable gel, first prepared by Brenzinger† and subsequently studied by Gortner and Hoffman, is formed when a hot alcoholic solution of dibenzoyl cystine is allowed to cool slowly. To prepare this gel, 0.2 gram of pure dibenzoyl cystine is dissolved in 5 cc. of hot 95 per cent alcohol, and while the solution is maintained at the boiling-point, hot water is slowly added until the volume of the solution becomes 100 cc. On cooling the solution,

* Grimaux, Compt. rend., **98**, 1540 (1884).

† Brenzinger, Zeit. physiol. Chem., **16**, 1537 (1892).

a transparent gel as rigid as a 5 per cent gelatin gel gradually forms. After some time opaque nuclei of stellate crystals appear. Although the gel has been found to contain 99.8 per cent of water, it nevertheless resembles a solid.

Another interesting gel is the calcium acetate gel employed by Baskerville as the basis of a process for the manufacture of "solid alcohol." If 85 cc. of 95 per cent alcohol be mixed rapidly with 15 cc. of a saturated aqueous solution of calcium acetate, the mixture almost immediately sets to a rigid gel. On applying a lighted match to the gel, it ignites and burns with a pale blue flame. On standing, the gel synerizes and numerous microscopic clusters of crystalline needles slowly deposit from the clear liquid.

In the course of an investigation of the properties of silicic acid gels, Holmes, Kaufman and Nicholas* prepared some remarkable vibrating gels. They added water-glass of 1.15 density to an equal volume of 6 N hydrochloric acid and poured the mixture into a heavy glass bottle until it was half filled, after which the bottle was corked and allowed to stand for several days. When the bottle and gel were tapped against a piece of wood, a rich musical tone was emitted. The gel formed when a similar mixture was poured into a bottle coated on the inside with vaseline, underwent marked contraction after setting, accompanied by copious syneresis. This gel was found to vibrate hardly any when tapped with a piece of wood.

Velocity of Imbibition. The rate at which gels imbibe water has been studied by Hofmeister.† The velocity of imbibition of water, by thin plates of gelatine and agar-agar, was measured by removing the immersed plates at definite intervals, and determining their increase in weight. Owing to the time consumed in making the weighings, the time intervals are affected by an appreciable error. The following table gives the data of a single experiment with gelatine.

If the weight of water imbibed in t minutes is w_t, and if w_∞ is the maximum weight of water which a gel can take up under the conditions, then the velocity of imbibition should be given by the equation,

$$\frac{dw}{dt} = k\,(w_\infty - w_t), \qquad (9)$$

* Holmes, Kaufman and Nicholas, Jour. Am. Chem. Soc., 41, 1329 (1919).

† Arch. exp. Pathol. u. Pharmakol., 27, 395 (1890).

which on integration becomes,

$$k = \frac{1}{t} \log_e \frac{w_\infty}{(w_\infty - w_t)}. \qquad (10)$$

The figures in the third column of the following table were calculated by means of this equation and, although the values are not strictly constant, the variation is no greater than might be expected where the experimental error is so large.

VELOCITY OF IMBIBITION IN GELATINE
(Thickness of plate 0.5 mm.)

Time (min.).	Water Imbibed (grams).	k.
5	3.08	0.090
10	3.88	0.084
15	4.26	0.084
20	4.58	0.064
25	4.67	0.075
∞	4.96	.....

Heat of Imbibition. The process of imbibition is accompanied by an evolution of heat. Quantitative measurements of the heat evolved when gels take up water have been made by Wiedemann and Lüdeking,* and also by Rodewald.† The following table gives Rodewald's data on the heat of imbibition of starch.

HEAT OF IMBIBITION OF STARCH
(Weight of dry starch 100 grams.)

Per Cent. Water.	Heat in Calories per Gram of Starch.
0.23	28.11
2.39	22.60
6.27	15.17
11.65	8.43
15.68	5.21
19.52	2.91

* Wied. Ann., **25**, 145 (1885).
† Zeit. phys. Chem., **24**, 206 (1897).

It will be observed, that the greatest development of heat accompanies the initial stages of imbibition, where very small amounts of water are taken up. This is what we might expect, when we remember, that it is the last remaining portion of water which is most difficult to remove from a gel, and that it is only through the application of heat that its complete removal can be effected.

Imbibition in Solutions. When a gel is immersed in a saline solution, the salt distributes itself between the solvent and the gel. The rate of imbibition is found to vary greatly according to the salt which is present in the solution. Thus, the velocity of imbibition has been found to be accelerated by the presence of the chlorides of ammonium, sodium and potassium, and also by the nitrate and bromide of sodium; on the other hand, the presence of the nitrate, sulphate and tartrate of magnesium retard imbibition.

The effect of acids and bases on imbibition appears to be similar to the influence of salts.

Adsorption. The tendency exhibited by all solids, to condense upon their surfaces a layer of any gas or liquid with which they may be in contact, is termed *adsorption*. The amount of adsorption is conditioned primarily by the extent of surface exposed, by the pressure and by the temperature. Under the same conditions of temperature and pressure, the amount of adsorption varies with the nature of the adsorbent and that of the adsorbed substance; in other words, adsorption is selective or specific.

At the surface of a solid surrounded by a gas or vapor, the phenomenon is generally known as gaseous adsorption, since any difference which may occur in the concentration of the solid phase is much too small to be detected. At the boundary between liquid and gaseous phases, the concentration of each phase undoubtedly undergoes alteration. In the case of the boundary between solid and liquid phases, the only apparent inequality in concentration occurs on the liquid side of the boundary, notwithstanding the fact that the adsorbed substance is quite commonly regarded as being bound to the surface of the solid phase. The cause of this erroneous conception is, that the extremely thin layer of liquid in which the alteration in concentration actually occurs, is the layer which wets the surface of the solid, and hence,

is the layer which adheres to the solid when it is removed from the liquid.

The retention of gases by charcoal is a typical example of gaseous adsorption, while the removal of coloring matter by charcoal, in the purification of various organic substances, may be cited as an example of adsorption of a liquid by a solid.

If the adsorbed substance increases in concentration in the vicinity of the boundary, the adsorption is said to be *positive;* if it decreases, the adsorption is said to be *negative.*

When any substance which presents a large extent of surface, such as charcoal, or filter paper, is brought in contact with a gas, or a solution, the process of adsorption is initiated, and will continue until a definite amount of substance has been adsorbed, or until *adsorption-equilibrium* has been attained.

Surface Concentration. It has been pointed out in an earlier chapter, that as the result of unbalanced molecular attraction, the surface of a liquid behaves like a tightly stretched membrane. In consequence of this contractile force, or surface tension, the pressure at the surface of a liquid is greater than the pressure within the liquid. Furthermore, when a dilute solution is unequally heated, the solute distributes itself in such a manner that the solution becomes more concentrated in the cooler portion. Just as the homogeneity of a dilute solution has been shown to be disturbed by inequality of temperature, so also inequality of pressure may be assumed to cause differences in concentration in the solution. Although direct experimental verification is difficult, there is abundant evidence for the view that the concentration at the surface of a solution differs from the volume-concentration of the solution, in consequence of the greater pressure in the surface layer.

The mathematical relation between surface concentration and surface tension was first deduced by J. Willard Gibbs* in 1876. The following simplified derivation of this important relation is due to Ostwald. Let s be the surface of a solution whose surface tension is γ, and let it be assumed that the surface contains 1 mol of the solute. If a very small portion of the solute enters the surface layer from the solution, thereby causing a diminution $d\gamma$, in the surface tension, the corresponding change in energy will be $s\,d\gamma$. But this amount of energy which is set free, must be equiva-

* Trans. Conn. Acad., Vol. III, 439 (1876).

lent to the osmotic work absorbed in effecting the removal of the same weight of solute from the solution. Let v be the volume of solution containing unit weight of solute, and let dp be the difference in the osmotic pressures of the solution before and after its removal: the osmotic work will be $-v\,dp$. Since the gain in surface energy and the osmotic work are equal, we have

$$s\,d\gamma = -v\,dp.$$

The solutions being dilute, we may assume that the gas laws hold, and since $v = RT/p$, we may write,

$$s\,d\gamma = -\frac{RT}{p}dp,$$

or

$$\frac{d\gamma}{dp} = -\frac{RT}{sp}.$$

Since pressure is directly proportional to concentration, the preceding equation becomes

$$\frac{d\gamma}{dc} = -\frac{RT}{sc}.$$

But s has already been defined as the surface which contains 1 mol of solute in excess; therefore it follows, that the excess of solute in unit surface is $1/s$. Writing $u = 1/s$, we have,

$$u = -\frac{c}{RT}\frac{d\gamma}{dc}, \tag{11}$$

which is the *equation of Gibbs*.

From this equation it is evident, that if the surface tension, γ, increases with the concentration, then u is negative, and the surface concentration is less than the concentration of the bulk of the solution. This is clearly negative adsorption. On the other hand, if γ decreases as the concentration increases, u is positive, and the surface concentration is greater than the concentration of the bulk of the solution, or the adsorption is positive. Finally, if the surface tension is independent of the concentration, then the concentration of the solute, in both the surface layer and the bulk of the solution, will be the same.

Adsorption of Gases. While, as yet, we possess no satisfactory method for determining the surface tension of a solid, yet there is

ordinary acceptation of the term. Neither can it be regarded as a purely physical combination, but rather as a more or less loose type of union, such as is attributed to the so-called "secondary valences" of the elements.

No very definite generalization concerning the behavior of adsorbents can be formulated. Charcoal, whether of vegetable or animal origin, is probably the most powerful adsorbent known. Silica gel, the dehydrated gel of silicic acid, is another effective adsorbent which seems destined to find extensive industrial applications.

Since adsorption diminishes as the temperature is raised, it follows that in order to obtain a large degree of adsorption a low temperature must be maintained. Thus, in removing the last traces of vapor in the production of high vacua, the apparatus to be exhausted is connected with a vessel cooled in liquid air and containing a good grade of adsorbent charcoal.

While our knowledge of the actual mechanism of the adsorption of a gas by a solid is rather meagre, nevertheless an interesting hypothesis based upon the unbalanced attraction of the atoms in the surface of the adsorbent has been advanced by Haber and also by Langmuir. As has been pointed out in a previous chapter (see p. 111) the atoms of a crystalline solid are located at definite points in a space-lattice, the crystal being held together by the mutual attractions of its atoms. Now while the atoms within the body of a crystal are completely surrounded by other atoms, it is evident that the atoms on the crystal surfaces are subject to a one-sided attraction only. The fields of force of the surface atoms are, therefore, only balanced toward the interior of the crystal, and it is suggested, that the residual attractive forces of the surface atoms, extending into the space occupied by the gas, are responsible for the phenomena of surface condensation.

Adsorption in Solution. The adsorption of dissolved substances bears a close resemblance to the adsorption of gases. Thus, if an aqueous solution of methylene blue be shaken with animal charcoal, the blue color of the solution almost completely disappears as a result of the adsorption of the dye by the charcoal. In like manner, a marked decrease in concentration is observed when an aqueous solution of amyl alcohol is agitated with charcoal. In both of these cases, equilibria are established which are entirely analogous to the equilibrium which results when carbon dioxide,

at a definite temperature and pressure, is passed over charcoal. Furthermore, the adsorption isotherm defines the relation of concentration to the quantity of solute adsorbed, in exactly the same manner as in the case of gaseous adsorption.

The values of the adsorption by charcoal of acetic acid in water, and of benzoic acid in water, at 25° C., are given in the following tables,* while the same data are presented graphically in Fig. 96.

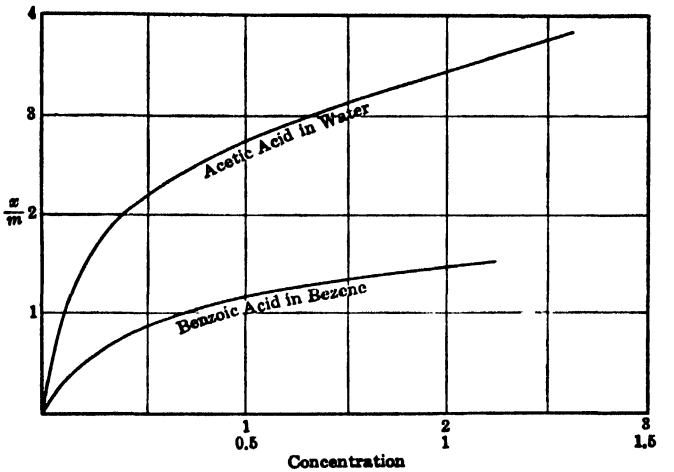


Fig. 96

ADSORPTION OF ACETIC ACID IN WATER BY CHARCOAL
TEMP. 25° C.

Concentration.	x/m.
0.018	0.467
0.031	0.624
0.0616	0.801
0.126	1.11
0.268	1.55
0.471	2.04
0.882	2.48
2.79	3.76

In order to test the validity of the adsorption isotherm, we plot the logarithms of the concentrations against the logarithms of the

* Freundlich, Kapillarchemie, pp. 147, 148.

ADSORPTION OF BENZOIC ACID IN BENZENE BY CHARCOAL
TEMP. 25° C.

Concentration.	x/m.
0.0062	0.437
0.025	0.78
0.053	1.04
0.118	1.44

ratio, x/m, where x is the mass, in grams, of the substance adsorbed, and m is the mass of the adsorbent. If the adsorption follows the exponential law expressed by the isotherm equation,

$$\left(\frac{x}{m}\right)^n = kc, \tag{13}$$

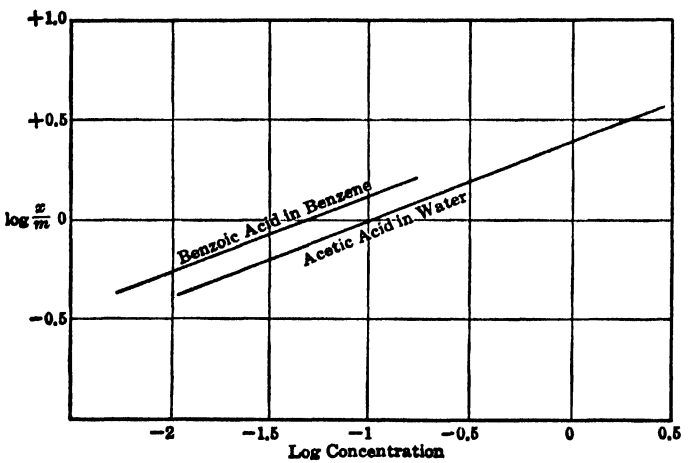


Fig. 97

the resulting curves should be rectilinear. It will be seen from the curves of Fig. 97 that the adsorption in both of the foregoing examples is accurately expressed by the isotherm equation.

It should be pointed out, however, that, as a rule, the adsorption isotherm applies only to dilute solutions. As the concentration is increased, the quantity of solute adsorbed tends to approach a constant limiting value, known as the *saturation value*. In extremely concentrated solutions, on the other hand, the adsorp-

tion falls below the saturation value. The reason for this apparent anomaly lies in the fact, that at higher concentrations the adsorption of the solvent becomes appreciable, and since we possess no reliable method for determining the extent to which the solvent is adsorbed, it follows that there is more or less uncertainty as to the values to be assigned to the ratio, x/m, in the isotherm equation.

In general, it may be said, that there is a close connection between adsorbability and solubility. Those substances which are readily soluble in a particular solvent are, as a rule, only slightly adsorbed from that solvent by charcoal, or other good adsorbents. On the other hand, substances which dissolve but sparingly in a given solvent are quite readily adsorbed. For example, fumaric acid is sparingly soluble in water while its isomer, maleic acid, is readily soluble; the adsorbability of the acids, however, is found to be in the reverse order of their solubilities.

The influence of temperature on adsorption in solutions is ordinarily very slight. In general, the adsorption becomes less as the temperature is increased, although many exceptions to this rule may be cited.

It has been found that adsorption is most pronounced with liquids having a high surface tension, such as water and sulphuric acid. This is in agreement with the view that adsorption is due to surface condensation. A further consequence of the surface condensation theory is, that the order of adsorbability is practically independent of the nature of the adsorbent. For example, the same order of adsorbability is preserved when a series of alcohols are shaken, first with charcoal, and then with talc, notwithstanding the fact that the former is fully five hundred times more active an adsorbent than the latter.

The general characteristics of adsorption in solutions may be briefly summarized as follows: —

(1) Adsorption in solutions is generally positive, i.e., on shaking a solution with a finely-divided adsorbent, the volume concentration of the solution will diminish.

(2) The amount of positive adsorption may be sufficient to remove almost all of the solute from a solution, especially if the solution is dilute. On the other hand, negative adsorption is always very small, and frequently is immeasurable.

(3) Adsorption is directly proportional to the so-called " spe-

cific surface," the latter term being defined as the ratio of the total surface of an adsorbent to its volume.

(4) On shaking a definite weight of an adsorbent with a given volume of solution of known concentration, a definite equilibrium will be established. If the solution is then diluted with a known amount of solvent, the adsorption will decrease until it acquires the same value which it would have attained, had the same weight of adsorbent been introduced directly into the more dilute solution. For example, if 1 gram of charcoal is agitated with 100 cc. of a 0.0688 molar solution of acetic acid for 20 hours, adsorption is found to reduce the original concentration of the acid to 0.0678 molar. In a second experiment, if 1 gram of charcoal is shaken for the same period of time with 50 cc. of $2 \times 0.0688 = 0.1376$ molar acetic acid, and then, after adding 50 cc. of water, the shaking is continued for an additional period of 3 hours, the final concentration of the acid will be found to be the same as in the first experiment.

(5) It is impossible to determine the specific surface of an adsorbent directly, owing to its porosity. However, according to (3), adsorption is directly proportional to the specific surface, and therefore, the weights of different adsorbents which produce the same amount of adsorption may be assumed to possess equal specific surfaces.

(6) Adsorption in solution is largely dependent upon the surface tension of the solvent. In solutions of the same substance in different solvents, the greatest adsorption occurs in that solution whose solvent possesses the highest surface tension.

(7) The order of efficiency of adsorption is not only generally independent of the nature of the solvent, but also of the nature of the adsorbed substance.

Exchange Adsorption. The phenomena attending the adsorption of suitable electrolytes by difficultly soluble salts, such as kaolin, are of special interest. If, for example, a solution of methylene-blue chloride, which is strongly ionized in aqueous solution, be shaken up with kaolin, the adsorption will be found to differ in several respects from the adsorption of a non-ionized solute by an insoluble adsorbent, such as charcoal. Thus, only the cation of the dye is adsorbed, while the chlorine ion remains behind in the solution with its concentration practically unaltered. Since the electrical neutrality of the solution must be preserved

through the presence of an equivalent number of cations and anions, the adsorption of the cations of methylene-blue must be offset by the removal from the adsorbent of an equivalent number of positively charged ions. In the example under consideration, electrical neutrality is found to be preserved by the removal of positively charged calcium ions from the kaolin. This type of adsorption is known as *exchange adsorption.* It should be observed, that this type of adsorption is polar in character, as distinguished from the adsorption of non-electrolytes, which is non-polar. Notwithstanding the differences between polar and non-polar adsorption, the two processes have been found, at low concentrations, to follow the exponential law expressed by the adsorption isotherm.

The behavior of artificial permutite affords an interesting example of exchange adsorption. This substance takes up calcium ions from solution and gives up an equivalent number of sodium ions; or under other conditions, a sodium permutite may give up nearly all of its sodium ions in exchange for silver ions. In the latter case, therefore, silver will have almost completely replaced sodium throughout the entire space lattice of the permutite.

These experiments would seem to indicate that siliceous adsorbents possess a more or less porous structure, and that even the silicate ions themselves may form an open frame-work through which the cations can freely circulate.

Adsorption undoubtedly plays an important rôle in both biological and physiological processes, the cell walls adsorbing dissolved substances in a manner quite analogous to the behavior of ordinary adsorbents. For example, it has been shown that the action of veratrine on the cardiac muscle of a certain variety of marine snail exhibits all of the characteristics typical of an adsorption. The drug is taken up quickly and reversibly, it can be removed by prolonged treatment with water, and the process follows the simple exponential law expressed by the adsorption isotherm.

The Theory of von Weimarn. As a result of a careful study of the experimental conditions controlling the formation and existence of the various types of colloids, von Weimarn* has formulated an interesting theory as to the process of formation of crystalline precipitates. In order to understand the theory of von Weimarn, let us consider the production of a precipitate in a

* Grundzüge der Dispersoidchemie (1911).

simple metathetical chemical reaction, taking place in aqueous solution. Let us assume that equivalent concentrations of two substances, which are non-associated in their respective solutions, react to form two other non-associated substances, one of which is precipitated, while the other remains in solution. Let L be the solubility, in mols per liter, of the precipitated substance, and let P be the number of mols of the precipitate which must separate from the supersaturated solution in order that its concentration may be reduced to the value, L mols per liter. Obviously, the ratio, P/L, is a measure of the degree of supersaturation of the solution. If η is the viscosity of the solution, then, according to von Weimarn, the character and degree of dispersion of the precipitate is given by the expression,

$$\delta = \frac{P}{L}\eta, \tag{14}$$

where δ is a quantity, known as the *dispersion coefficient*. When a series of precipitations are carried out in such a manner that the value of δ is the same in each case, the precipitates are said to be formed under "corresponding conditions." According to von Weimarn, the law governing precipitation under corresponding conditions may be expressed as follows: — The general character and the degree of dispersion of crystalline precipitates are always the same, provided precipitation takes place under corresponding conditions.

The significance of this important principle and the application of equation (14) to a typical precipitation, may be illustrated by tabulating the results obtained by von Weimarn, on precipitating barium sulphate from mixtures of aqueous solutions of barium thiocyanate and manganous sulphate, over a wide range of concentrations.

It is evident, therefore, that the degree of dispersion of the precipitate is greatest when low and high concentrations of the reagents are employed, and that the particles of the precipitate attain their maximum size in the region of medium concentration.

Preparation of Colloidal Solutions. Since 1861, when Graham published his first paper on colloids, numerous investigators have devised methods for the preparation of colloidal solutions. Within recent years our knowledge of this class of solutions has been greatly increased, many crystalloidal substances having been

VARIATION IN NATURE OF $BaSO_4$ WITH CONDITIONS OF PRECIPITATION

Equiv. Conc. of Reagents.	P gm. per 100 cc.	δ.	Nature of Precipitate.
0.00005 to 0.00014	0 0.0006	0 3	No ppt. in a year — micro-crystals to be expected in a few years.
0.00014 to 0.0017	0.0006 0.0096	3 48	Slow pp'tion at $\delta = 8$. Suspensoid stage at $\delta = 25$ (momentary). Complete separation in months to hours.
0.0017 to 0.75	0.0096 4.38	48 21900	Precipitation in few seconds at $\delta = 48$. Beyond this, instantaneous precipitation. Crystal skeletons and needles. At $\delta =$ 21900, crystals barely visible.
0.75 3	4.38 17.51	21900 87500	Immediate formation of amorphous precipitates.
3 to 7	17.51 40.9	87500 204500	Cellular, clear jelly.

obtained in the colloidal condition. As a result of these investigations, we no longer speak of crystalloidal and colloidal matter, but use the terms, crystalloid and colloid, to distinguish two different states. In fact, it is now recognized that it is simply a matter of overcoming certain experimental difficulties, before it will be possible to obtain all forms of matter in the colloidal state. The scope of this book forbids a detailed account of the various methods which have been devised for the preparation of colloidal solutions.* We must confine ourselves, therefore, to a general classification of the methods by which colloidal, or disperse systems are produced.

The various methods for the production of colloidal systems may conveniently be divided into two classes, as follows: (1) Methods in which relatively coarse material is subdivided into fine particles, and (2) methods in which the minute particles, molecules, or atoms of a substance are gathered together to form particles of

* See "Die Methoden zur Herstellung Kolloider Lösungen anorganischer Stoffe," by The Svedberg, Dresden, 1909. Also "The Formation of Colloids," by the same author.

colloidal dimensions. Methods belonging to the first class are termed "dispersion methods," while those belonging to the second class are known as "condensation methods." In dispersion methods the relative surfaces of the systems are increased, whereas in condensation methods the relative surfaces are decreased. In general, it may be said, that condensation processes are more common than dispersion processes.

It is not always possible, at first sight, to determine whether a given process involves dispersion, or condensation. For example, when a colloidal sol is prepared by forming an electric arc between two metal wires immersed in a liquid, the metal is at first vaporized by the arc, and subsequently condenses to form particles of larger dimensions.

The Colloid Mill. The so-called "colloid mill"* is one of the most important and promising devices for the production of colloidal solutions by the dispersion method. The substance to be dispersed is suspended in the dispersion medium in the form of coarse particles. The suspension is then introduced into the colloid mill, where an exceedingly high velocity is imparted to one portion of the suspension, while the other portion either remains at rest, or is caused to rotate at high speed in a direction opposite to that of the first portion. This is accomplished by passing the liquid through a channel in a shaft on which two metal discs rotate at high speed in opposite directions. As the suspension flows out in a thin layer between the two oppositely rotating discs, the suspended particles are subjected to an intense shearing stress under which they rapidly disintegrate. In order to produce a high degree of dispersion, a peripheral speed of 30 m. per second has been found necessary. All previous attempts to produce colloidal systems by purely mechanical means have failed, but the success of the colloidal mill seems to warrant the belief that it will find extensive application in the industrial production of colloids.

Condensation Methods. In 1897, Bredig† discovered, while studying the action of the electric current on different liquids, that if an arc is established between two metallic wires immersed in a liquid, minute particles of metal are torn off from the negative terminal and remain suspended in the liquid indefinitely. In

* See article by A. W. Kenney, Chem. Met. Eng., 27, 1080 (1922).

† Zeit. Elektrochem., 4, 514 (1897); Zeit. phys. Chem., 31, 258 (1899).

order to prepare a colloidal solution by the method of electrical dispersion, Bredig recommends that a direct current arc be established between wires of the metal of which a colloidal solution is desired, the ends of the wires being submerged in water in a well-cooled vessel, as shown in Fig. 98. The current employed ranges in strength from 5 to 10 amperes, and the voltage lies between 30 and 110 volts. A rheostat and an ammeter are included in the circuit.

The wires are brought in contact for an instant in order to establish the arc, after which they are separated about 2 mm. Clouds of colloidal metal are projected out into the water from the negative wire, portions of the metal torn off being distributed through the water as a coarse suspension. The size of the particles disrupted from the negative terminal is dependent upon the strength of the current, a current of 10 amperes producing a greater proportion of colloidal metal than a current of 5 amperes. The addition of a trace of potassium hydroxide to the water has been found to stabilize the dispersed metal. When gold wires are used, deep red colloidal solutions are obtained, which, after standing for several weeks, acquire a bluish-violet color. With extra precautions, the red colloidal gold solutions may be preserved for two years. These solutions have been shown by Bredig to contain about 14 mg. of gold per 100 cc. In this manner, Bredig prepared colloidal solutions of platinum, palladium, iridium, and silver.

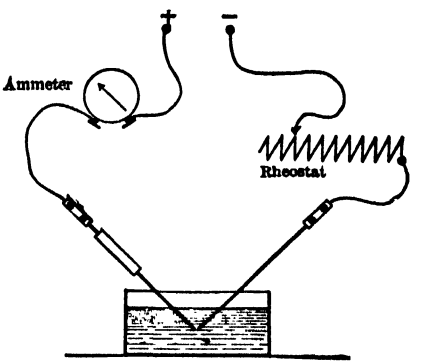


Fig. 98

Svedberg and his co-workers,* as the result of a closer study of the direct current arc, have shown that the production of metallic vapor can be greatly increased by protecting the electrodes from the cooling effect of the surrounding liquid. The colloidal particles in sols obtained with the protected arc have an average diameter of 5 $m\mu$, while those produced with the unprotected arc are approximately 25 $m\mu$ in diameter. Spectro-

* Svedberg, Formation of Colloids, p. 25.

grams of the free arc reveal that relatively little of the dispersion medium is decomposed in the case of the protected arc.

By means of an oscillatory arc, Svedberg and his pupils have also succeeded in preparing sols of all available metals, including those of the alkalis. In the case of the latter, ether, free from water and oxygen, is employed as the dispersion medium.

Other condensation methods than the electrical method are those based on the formation of the disperse phase by purely chemical means. These are probably the most important methods which we possess for the preparation of colloidal solutions. The chemical methods may be conveniently classified according to the type of reaction involved. Thus, we distinguish four different processes as follows: (1) Reduction processes, (2) Oxidation processes, (3) Dissociation processes, and (4) Metathetic processes. A single example of each type of process will here be given.

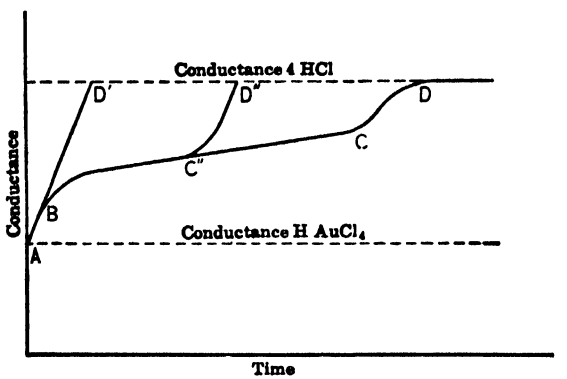


Fig. 99

(1) *Reduction Processes.* One of the most thoroughly investigated reactions of this type is the reduction of chlorauric acid by means of hydrogen peroxide. According to the equation,

$$2\,HAuCl_4 + 3\,H_2O = 2\,Au + 8\,HCl + 3\,O_2,$$

it is evident that four molecules of hydrochloric acid are formed for every molecule of chlorauric acid reduced. This reaction has been studied by measuring the change in the electrical conductance of the reaction mixture with time. The time-conductance curve, shown in Fig. 99, sheds much light on the mechanism of the

process of colloid formation. If no particles of gold are present in the mixture, the conductivity rises rapidly along AB, while the intensity of the color of the mixture decreases. Following the sudden rise, AB, the conductivity continues to increase gradually from B to C, beyond which point it rises rapidly to the limiting value D, corresponding to the conductance of 4 HCl. The characteristic red color of the gold sol appears at C, and continues to deepen along CD. When the sol is examined under the ultramicroscope, only a very small number of particles are visible during the period represented by BC. At C there is a sudden appearance of particles which continue to increase in number as the curve CD is traversed. If gold particles are introduced into the chlorauric acid initially, before the reducing agent is added, the reduction then proceeds along the nearly straight line, BD'. In like manner, if gold particles be added during the reduction period, the velocity of the reaction instantly changes and the process follows the curve, $C''D''$, to completion. The probable interpretation of the foregoing experiment is, that upon adding hydrogen peroxide to a solution of chlorauric acid, about 30 per cent of the solute is reduced to gold molecules, thereby forming a highly supersaturated solution of gold in water. This of course is in accord with the reaction equation. The gold molecules now slowly condense to colloidal particles along BC until, when C is reached, most of the particles will have attained the minimum size of nuclear action, or in other words are capable of acting as centers of crystallization. The reduction now proceeds rapidly to completion, the remainder of the gold depositing on the nuclei formed during the period represented by BC.

(2) *Oxidation Processes.* As an example of an oxidation process, we may cite the reaction between hydrogen sulphide and sulphur dioxide, as represented by the equation,

$$2\,H_2S + SO_2 = 3\,S + 2\,H_2O.$$

The reaction has been thoroughly investigated by Odén,* who found, when hydrogen sulphide gas is passed into a solution of sulphur dioxide, that at high concentrations the reaction does not follow the simple equation just given, but that pentathionic and other thio acids are formed along with sulphur. Nevertheless,

* Odén, Nova Acta, Upsala (4), 3, No. 4 (1913).

starting with a 1.8 *N* solution of sulphur dioxide, he obtained a sol containing approximately 8 grams of sulphur per 100 cc. of solution.

(3) *Dissociation Processes.* Dissociation processes are of very limited use in the preparation of colloidal solutions, but notwithstanding this fact, they recently have acquired importance because of their probable relation to the formation of the so-called " latent image " in the sensitized emulsion of the photographic plate. An interesting example of this type of process is afforded by nickel carbonyl. If a solution of this compound in benzene is heated, dissociation occurs according to the equation,

$$Ni(CO)_4 = Ni + 4\,CO.$$

The resulting nickel sol is either brown, or black, in color and resembles closely the nickel sols obtained by electrical pulverization.

(4) *Metathetical Processes.* A large number of reactions involving metathesis, or double decomposition, have been shown to give rise to colloidal solutions. The most important of these are the following:

(1) Formation of *oxide* sols by
  (*a*) Hydrolysis.
  (*b*) Precipitation with alkalis.
  (*c*) Decomposition of salts by acids.
(2) Formation of *sulphide* sols by
  Precipitation with hydrogen sulphide.
(3) Formation of *salt* sols by precipitation with easily soluble
  (*a*) Halides.
  (*b*) Sulphates.
  (*c*) Chromates.
  (*d*) Phosphates.
  (*e*) Ferro- and ferri-cyanides.

The formation of colloidal arsenious sulphide, by treating arsenious oxide with hydrogen sulphide, affords a good example of this type of process. The reaction is represented by the equation

$$As_2O_3 + 3\,H_2S = As_2S_3 + 3\,H_2O.$$

By varying the concentration of the solution of arsenious oxide, the opacity of the resulting sol can be altered. It has been proven

that arsenious sulphide sols are built up of particles varying in size, and that sols prepared from dilute solutions of arsenious oxide contain smaller particles than those derived from concentrated solutions.

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CHAPTER XI

THERMOCHEMISTRY

General Introduction. A chemical reaction is almost invariably accompanied by a thermal change. In the majority of cases heat is evolved; a violent reaction developing a large amount of heat, while a feeble reaction develops a comparatively small amount. Such reactions are said to be *exothermic.* A relatively small number of chemical reactions are known which take place with an absorption of heat. These are termed *endothermic* reactions. Instances of chemical reactions unaccompanied by any thermal change are very rare, and are almost wholly confined to the reciprocal transformations of optical isomers. These facts, which were first observed by Boyle and Lavoisier, led to the view, that the amount of heat evolved in a chemical reaction might be taken as a measure of the chemical affinity of the reacting substances. However, with the advance of our theoretical knowledge, it is now known that this is not true, although a parallelism between heat evolution and chemical affinity frequently exists.

Thermochemistry is concerned with the thermal changes which accompany chemical reactions.

Thermal Units. Heat is a form of energy, and, like other forms of energy, it may be resolved into two factors; an intensity factor, the temperature, and a capacity factor, the entropy. The product of these two factors, the thermal energy, may be measured in terms of any one of several units among which those defined below are most frequently employed.

The *small calorie* (cal.) is the quantity of heat required to raise the temperature of 1 gram of water from 15° C. to 16° C. The temperature interval is specified because the specific heat of water varies with the temperature. The *large or kilogram calorie* (Cal.), is the quantity of heat required to raise the temperature of 1000 grams of water from 15° C. to 16° C. The *Ostwald or average calorie* (K), is the quantity of heat required to raise the temperature of 1 gram of water from the melting-point of ice to the boiling-point of water, under a pressure of 760 mm. of mercury. It

is approximately equal to 100 cal., or to 0.1 Cal. The *joule* (j), a unit based on the C.G.S. system, is equal to 10^7 ergs. This being inconveniently small is generally multiplied by 1000, giving the *kilojoule* (J), which is, therefore, equal to 10^{10} ergs. The last two units are open to the objection that their values are dependent upon the mechanical equivalent of heat, any change in the accepted value of which would involve a correction of the unit of heat. The different capacity factors of heat energy are related as follows: —

1 cal. = 0.001 Cal. = 0.01 K (approx.) = 4.183 j = 0.004183 J.

Thermochemical Equations. In order to represent the changes in energy which accompany chemical reactions, an additional meaning has been assigned to the chemical symbols. As ordinarily used, these symbols represent only the molecular or formula weights of the reacting substances. In a thermochemical or energy equation the symbols represent, not only the weight in grams expressed by the formula weights of the substances, but also the amount of heat energy contained in the formula weight in one state as compared with the energy contained in a standard state. For example, the energy equation,

$$C + 2\,O = CO_2 + 94{,}300 \text{ cal.},$$

indicates that the energy contained in 12 grams of carbon and 32 grams of oxygen, exceeds the energy contained in 44 grams of carbon dioxide, at the same temperature, by 94,300 calories.* In writing energy equations, it is very essential that we have some means of distinguishing between the different states of aggregation of the reacting substances, since the energy content of a substance is not the same in the gaseous, liquid, and solid states. In the system proposed by Ostwald, ordinary type is used for liquids, heavy type for solids, and italics for gases. Another and more convenient system has been proposed, in which solids are designated by enclosing the symbol, or formula, within square brackets; liquids by the simple, unbracketed symbol, or formula; and gases by enclosing the symbol, or formula, within parentheses. The above equation should, therefore, be written in the following manner:

$$[C] + (2\,O) = (CO_2) + 94{,}300 \text{ cal.}$$

* Note that in this chapter, only, the positive sign indicates *evolution* of heat.

Thermochemical Measurements. In order to measure the number of calories evolved, or absorbed, when substances react, it is necessary that the reaction should proceed rapidly to completion. This condition is fulfilled by two classes of processes. In the first class, we may mention the processes of solution, hydration, and neutralization; and in the second class, the process of combustion.

The apparatus used for measuring the capacity factor of heat energy is a *calorimeter*. This instrument consists, essentially, of a large insulated vessel containing a weighed amount of water, and a smaller submerged vessel, or reaction chamber, within which the reaction, whose thermal effect is sought, is allowed to take place. By observing the rise in temperature of the water accompanying the reaction, and knowing the heat capacities of the calorimeter and its accessories, it is possible to calculate the amount of heat evolved, or absorbed, in the reaction. This instrument may be given a variety of forms, depending upon the particular use to which it is to be put.

The Combustion Calorimeter. The combustion of many substances, such as organic compounds, proceeds very slowly in air under ordinary pressures. Such reactions can be accelerated, if they are caused to take place in an atmosphere of compressed oxygen. For this purpose the combustion calorimeter was devised by Berthelot.* In this apparatus the essential feature is the so-called *combustion bomb*, shown in Fig. 100. This consists of a strong cylinder of a special acid-resisting alloy, which is furnished with a heavy threaded cover. The substance to be burned is placed in a platinum capsule fastened to appropriate supports, while a weighed piece of fine iron wire, the middle portion of which dips into the substance, is connected with electric terminals on the cover of the bomb. The cover is screwed down tight, and the bomb is filled with oxygen, under a pressure of from 20 to 25 atmospheres. The bomb is then submerged in the calorimeter, as shown at *B* in Fig. 101. The mass of water in the calorimeter being known,

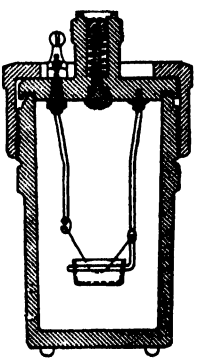

Fig. 100

* Ann. Chim. Phys. (5), 23, 160 (1881); (6), 10, 433 (1887).

and its temperature having been read, an electric current is passed through the iron wire in the bomb, causing it to burn

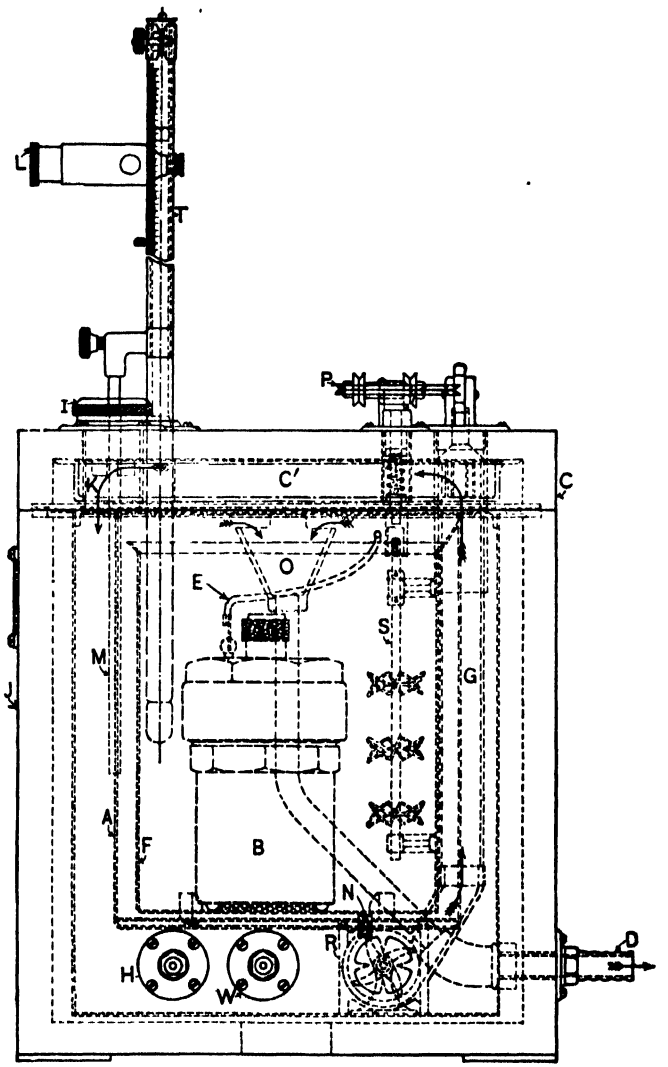

Fig. 101

and thus ignite the substance. The rise in temperature, due to the combustion, is observed, and the quantity of heat evolved is calculated. Corrections must be applied for the heat evolved

from the combustion of the iron, and for the heat evolved from the oxidation of the nitrogen of the residual air in the bomb.

The calorimeter, shown in Fig. 101, is of the so-called "adiabatic" type in which the temperature of the jacketing water is constantly maintained at the same temperature as that of the water in the calorimeter itself, thereby eliminating the troublesome and uncertain correction for loss of heat by radiation. In the instrument illustrated in Fig. 101, water is circulated by means of the stirrer, S, which includes a small turbine for directing a portion of the water upward in G, and thence through the cover C'. In this manner the jacketing water is uniformly distributed around the vessel, F, and the bomb, B. The control of the temperature is accomplished by having available a supply of both hot and cold water, the latter coming directly from the laboratory tap, while the former is furnished by a small heater, (not shown in the diagram), located at the right of the apparatus. The hot and cold inlets are so placed that the control cocks are easily operated by one hand.*

Law of Lavoisier and Laplace. In 1780, Lavoisier and Laplace,† as a result of their thermochemical investigations, enunciated the following law: — *The quantity of heat which is required to decompose a chemical compound is precisely equal to that which was evolved in the formation of the compound from its elements.* This first law of thermochemistry will be seen to be a direct corollary of the law of the conservation of energy, first clearly stated by Mayer in 1842.

Law of Constant Heat Summation. A generalization of fundamental importance to the science of thermochemistry was discovered, in 1840, by Hess.‡ He pointed out, that *the heat evolved in a chemical process is the same whether it takes place in one, or in several steps.* This is known as *the law of constant heat summation.* The truth of the law may be illustrated by the equality of the heat of formation of ammonium chloride in aqueous solution, when prepared in two different ways.

* For further data on adiabatic calorimetry see the following papers: Richards and Burgess, Jour. Am. Chem. Soc., **32**, 431 (1910); Benedict and Higgins, ibid., **32**, 461 (1910).

† Oeuvres de Lavoisier, Vol. II, p. 283.

‡ Pogg. Ann., **50**, 385 (1840).

Thus,

(A)

$$(NH_3) + (HCl) = [NH_4Cl] \quad + 42{,}100 \text{ cal.}$$
$$[NH_4Cl] + aq. = NH_4Cl, aq. \quad - 3{,}900 \text{ cal.}$$
$$38{,}200 \text{ cal.}$$

(B)

$$(NH_3) + aq. = NH_3, aq. \quad + 8{,}400 \text{ cal.}$$
$$(HCl) + aq. = HCl, aq. \quad + 17{,}300 \text{ cal.}$$
$$NH_3, aq. + HCl, aq. = NH_4Cl, aq. \quad + 12{,}300 \text{ cal.}$$
$$38{,}000 \text{ cal.}$$

It will be observed, that the total amount of heat evolved in the formation and solution of ammonium chloride is the same, within the limits of experimental error, whether gaseous ammonia and hydrochloric acid are allowed to react, and the resulting product is dissolved in water; or, whether the gases are each dissolved separately, and then allowed to react. It should be noted, that when a substance is dissolved in so large a volume of water, that the addition or removal of a small portion of solvent produces no thermal effect, it is customary to denote it by the symbol aq. (Latin *aqua* = water.) Thus,

$$NH_4Cl, aq. + nH_2O = NH_4Cl, aq.,$$
$$NH_4Cl, aq. - nH_2O = NH_4Cl, aq.$$

By means of the law of constant heat summation, it is possible to find indirectly the amount of heat developed, or absorbed, by any reaction, even though it is impossible to carry it out experimentally. For example, it is impossible to measure the heat evolved when carbon burns to carbon monoxide. But the heat evolved when carbon monoxide burns to carbon dioxide, and also the heat evolved when carbon burns to carbon dioxide, can be accurately determined. The energy equations are as follows: —

$$[C] + 2\,(O) = (CO_2) + 94{,}300 \text{ cal.} \quad (1)$$
$$(CO) + (O) = (CO_2) + 67{,}700 \text{ cal.} \quad (2)$$

Treating these equations algebraically, and subtracting equation (2) from equation (1), we have

$$[C] + (O) = (CO) + 26{,}600 \text{ cal.},$$

or, the heat of combustion of carbon to carbon monoxide is 26,600 calories. Again, as a further illustration of the applicability of the law of Hess, we may take the calculation of the heat of formation of hydriodic acid from its elements, making use of the following energy equations: —

$$2\,KI,\,aq. + 2\,(Cl) = 2\,KCl,\,aq. + 2\,[I] + 524\,K \quad (3)$$
$$2\,HI,\,aq. + 2\,KOH,\,aq. = 2\,KI,\,aq. + 2\,H_2O + 274\,K \quad (4)$$
$$2\,HCl,\,aq. + 2\,KOH,\,aq. = 2\,KCl,\,aq. + 2\,H_2O + 274\,K \quad (5)$$
$$2\,(HI) + aq. = 2\,HI,\,aq. + 384\,K, \quad (6)$$
$$2\,(HCl) + aq. = 2\,HCl,\,aq. + 346\,K, \quad (7)$$
$$2\,(H) + 2\,(Cl) = 2\,(HCl) + 440\,K, \quad (8)$$

adding equations (3) and (4),

$$2\,(Cl) + 2\,HI,\,aq. + 2\,KOH,\,aq. = 2\,KCl,\,aq. + 2\,[I] + 2\,H_2O + 798\,K. \quad (9)$$

Subtracting equation (5) from equation (9),

$$2\,(Cl) + 2\,HI,\,aq. - 2\,HCl,\,aq. = 2\,[I] + 524\,K,$$

or

$$2\,(Cl) + 2\,HI,\,aq. = 2\,[I] + 2\,HCl,\,aq. + 524\,K, \quad (10)$$

adding equations (6) and (10),

$$2\,(HI) + aq. + 2\,(Cl) = 2\,[I] + 2\,HCl,\,aq. + 908\,K, \quad (11)$$

subtracting equation (7) from equation (11),

$$2\,(HI) + 2\,(Cl) - 2\,(HCl) = 2\,[I] + 562\,K,$$

or

$$2\,(HI) + 2\,(Cl) = 2\,[I] + 2\,(HCl) + 562\,K, \quad (12)$$

subtracting equation (8) from equation (12),

$$2\,(HI) - 2\,(H) = 2\,[I] + 122\,K, \quad (13)$$

or

$$2\,(H) + 2\,[I] = 2\,(HI) - 122\,K. \quad (14)$$

In a similar manner, practically any heat of formation may be calculated, provided the proper energy equations are combined.

Heat of Formation. The intrinsic energy of the substances entering into chemical reaction is unknown, the amount of heat evolved, or absorbed, in the process being simply a measure of the difference between the energy of the reacting substances and the energy of the products of the reaction. Thus, in the equation,

$$[C] + 2\,(O) = (CO_2) + 94{,}300 \text{ cal.},$$

the difference between the energy of a mixture of 12 grams of carbon and 32 grams of oxygen, on the one hand, and the energy of 44 grams of carbon dioxide, on the other, is seen to be 94,300 calories. The equation is clearly incomplete, since we have no means of determining the intrinsic energies of free carbon and oxygen. Furthermore, since the elements are not mutually convertible, we have no means of determining the difference in energy between them. It is customary, therefore, in view of this lack of knowledge, to put the intrinsic energies of the elements equal to zero.

If the heats of formation of the substances present in a reaction are known, it is much simpler to substitute these in the energy equation, and solve for the unknown term. This method avoids the laborious process of elimination from a large number of energy equations, as in the preceding examples. If all of the substances involved in a reaction are considered as decomposed into their elements, it is evident that the final result of the reaction will be the difference in the sums of the heats of formation on the two sides of the equation. This leads to the following rule: — *To find the quantity of heat evolved, or absorbed, in a chemical reaction, subtract the sum of the heats of formation of the substances initially present, from the sum of the heats of formation of the products of the reaction, placing the heat of formation of all elements equal to zero.*

The energy equation for the formation of carbon dioxide from its elements may then be written as follows: —

$$0 + 0 = (CO_2) + 94{,}300 \text{ cal.},$$

or

$$(CO_2) = -\,94{,}300 \text{ cal.}$$

Therefore, in writing an energy equation we make use of the following rule: — *Replace the formulas of each compound in the reac-*

tion equation by the negative values of their respective heats of formation, and solve for the unknown term. This unknown term may be either the heat of a reaction, or the heat of formation of one of the reacting substances. The following examples will serve to illustrate the application of the above rules: —

(1) Let it be required to find the heat of the following reaction

$$[MgCl_2] + 2\,[Na] = 2\,[NaCl] + [Mg] + x,$$

where x is the heat of the reaction. The heat of formation of $MgCl_2$ is 151 Cal., and that of NaCl is 97.9 Cal., therefore,

$$-151 + 0 = -(2 \times 97.9) + 0 + x,$$

or

$$x = 44.8 \text{ Cal.}$$

(2) The heat of combustion of 1 mol of methane is 213.8 Cal., and the heats of formation of the products, carbon dioxide and water, are 94.3 Cal. and 68.3 Cal., respectively. Let it be required to find the heat of formation of methane. Representing the heat of formation of methane by x, we have

$$(CH_4) + 2\,(O_2) = (CO_2) + 2\,H_2O + 213.8 \text{ Cal.},$$
$$-x + 0 = -94.3 - 2 \times 68.3 + 213.8,$$

or

$$x = 17.1 \text{ Cal.}$$

(3) The heat of combustion of 1 mol of carbon disulphide is 265.1 Cal., the thermochemical equation being,

$$CS_2 + 3\,(O_2) = (CO_2) + 2\,(SO_2) + 265.1 \text{ Cal.}$$

The heats of formation of carbon dioxide and sulphur dioxide are 94.3 Cal. and 71 Cal., respectively. The heat of formation of carbon disulphide, x, may then be calculated as follows:

$$-x + 0 = -94.3 - 2 \times 71 + 265.1,$$

or

$$x = -28.8 \text{ Cal.}$$

Carbon disulphide is thus seen to be an endothermic compound.

The heats of formation of a number of metallic and non-metallic compounds are given in the accompanying table.

HEATS OF FORMATION *
(METALLIC COMPOUNDS)

Oxides

Na_2O	97,100 cal.
K_2O	91,000
CaO	145,000
BaO	133,400
MgO	143,600
ZnO	85,440
FeO	65,700
Fe_2O_3	197,000
Fe_3O_4	270,800
PbO	50,300
CuO	37,200
Ag_2O	5,900–7,000
HgO	21,500

Sulphides

Na_2S	89,300 cal.
K_2S	103,500
CaS	90.800
CuS	10,000
PbS	18,400

Chlorides

$NaCl$	97,700 cal.
KCl	105,600
$BaCl_2$	196,900
$MgCl_2$	151,000
$ZnCl_2$	97,200
$FeCl_2$	82,050
$FeCl_3$	96,040
$CuCl_2$	51,630
$AgCl$	29,900
$PbCl_2$	82,800

Bromides

$NaBr$	85,700 cal.
KBr	95,300
$AgBr$	22,700
$PbBr_2$	64,450

Iodides

NaI	61,900 cal.
KI	80,130
CuI	16,300
AgI	15,000
PbI_2	39,800

Nitrates

$NaNO_3$	111,000 cal.
KNO_3	119,000
$Ba(NO_3)_2$	228,000
$AgNO_3$	28,740
$Pb(NO_3)_2$	105,500

Sulphates

Na_2SO_4	328,590 cal.
K_2SO_4	344,300
$BaSO_4$	340,000
$MgSO_4$	302,000
$ZnSO_4$	229,600
$CuSO_4$	182,600
Ag_2SO_4	167,300
$PbSO_4$	216,210

(*Non-metallic Compounds*)

HCl	22,000 cal.
HBr	8,440
HI	−6,040
H_2O (liq.)	68,380
H_2O (gas)	58,000
NH_3	11,890
SO_2	71,080
H_2SO_4	192,920
N_2O	−17,740
NO	−21,570
HNO_3	41,600
CO	29,000
CO_2	96,960
CH_4	21,750
C_2H_2	−47,770
C_6H_6	−12,510

* Data compiled from Physikalish-chemische Tabellen, Landolt-Börnstein-Meyerhoffer.

Heat of Solution. The thermal change accompanying the solution of 1 mol of a substance, in so large a volume of solvent that subsequent dilution of the solution causes no further change in temperature, is termed the *heat of solution at infinite dilution.* The solution of neutral salts is generally an endothermic process. This fact may be readily accounted for, on the hypothesis that considerable heat

must be absorbed, as heat of fusion and heat of vaporization, before the solid salt can assume a condition in solution which closely resembles that of a gas. The heat of solution of hydrated salts is less than the heat of solution of the corresponding anhydrous salts. For example, the heat of solution of 1 mol of anhydrous calcium nitrate is 4000 calories, while the heat of solution of 1 mol of the tetrahydrate is −7600 calories.

The difference between the heats of solution of the anhydrous and hydrated salts is termed the *heat of hydration*. The heats of solution in water of some of the more common compounds are given in the following table, the values being expressed in small calories.

HEATS OF SOLUTION

Substance	Mols H_2O	Q	Substance	Mols H_2O	Q
HCl	300	+ 17,315 cal.	NaBr	200	− 190 cal.
HBr	400	+ 19,940	$NaBr.2H_2O$	300	− 4,710
HI	500	+ 19,210	NaI	200	+ 1,220
NH_3	200	+ 8,430	$NaI.2H_2O$	300	− 4,010
H_2SO_4	1600	+ 17,850	NaOH	200	+ 9,940
HNO_3	300	+ 7,480	$NaNO_3$	200	− 5,030
NH_4Cl	200	− 3,880	Na_2SO_4	400	+ 460
NH_4NO_3	200	− 6,320	$Na_2SO_4\ 10H_2O$	400	− 18,760
NaCl	100	− 1,180	KCl	200	− 4,440
$Ca(OH)_2$	2500	+ 2,790	KBr	200	− 5,080
$CaCl_2$	300	+ 17,410	KI	200	− 5,110
$CaCl_2.6H_2O$	400	− 4,310	KOH	250	+ 13,290
$ZnSO_4$	400	+ 18,430	KNO_3	200	− 8,520
$ZnSO_4\ 7H_2O$	400	− 4,260	K_2SO_4	400	− 6,380
$CuCl_2$	600	+ 11,080	$CuSO_4$	400	+ 15,800
$CuCl_2.2H_2O$	400	+ 4,210	$CuSO_4.5H_2O$	400	− 2,750

Heat of Dilution. The *heat of dilution* of a solution is the quantity of heat which is evolved, or absorbed, per mol of solute when the solution is greatly diluted. Beyond a certain dilution, further addition of solvent produces no thermal change. While there is a definite heat of solution for a particular solute in a particular solvent, the heat of dilution remains indefinite, since the latter is dependent upon the degree of dilution. Those gases which obey Henry's law, are practically the only substances which have no appreciable heats of solution, or dilution.

The following tables give the heats of dilution of several acids and bases.

HEATS OF DILUTION OF ACIDS

Mols of Water to 1 mol Acid	HCl	HNO_3	H_2SO_4
1	5,370 cal.	3,340 cal.	6,380 cal.
2	11,360	4,860	9,420
5	14,960	6,600	13,110
8	.....	7,220	.....
10	16,160	7,270	14,950
20	16,760	7,360	16,260
50	17,100	.....	16,700
100	17,200	7,210	16,900
200	.....	7,180	17,100
300	17,300	.....	.....
800	.....	.....	17,600
1600	.....	.....	17,900

HEATS OF DILUTION OF BASES

Mols of Water Added	To $KOH + 3\ H_2O$	To $NaOH + 3\ H_2O$
2	1500 cal.	2130 cal.
4	2100	2890
6	2360	3100
17	2700	3080
47	2740	3100
97	2750	3000
197	2750	2940

It is apparent, that as the dilution of the above solutions is increased, the thermal effect produced by the addition of more solvent becomes less and less, and ultimately becomes zero. This is shown diagrammatically in Fig. 102, in which the abscissæ represent the composition of the solutions, and the ordinates represent the corresponding heats of solution. The ordinates, An_1 and Bn_2, are the heats of solution of one mol of A, in n_1 and n_2 mols of B, respectively. The difference between these two heats of solution is represented by BC: this is the so-called "integral

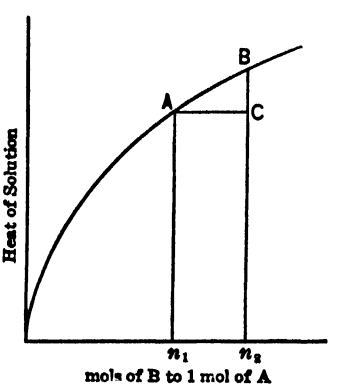

Fig. 102

heat of dilution," corresponding to an increase in the number of mols of B, from n_1 to n_2. If one mol of B is added to a large volume of solution, containing one mol of A in n_1 mols of B, the resulting thermal change is called the "differential heat of dilution," and will be represented by the tangent to the curve at A.

Reactions at Constant Volume. When a chemical reaction takes place without any change in volume, or when the external work, resulting from a change in volume, is not included in the heat of the reaction, the process is said to take place at constant volume. That is to say, the condition of constant volume, is a condition which involves no external work, either positive, or negative. Under these conditions, the total energy of the reacting substances is equal to the total energy of the products of the reaction, plus the quantity of heat developed by the reaction.

Reactions at Constant Pressure. When a chemical reaction is accompanied by a change in volume, the system suffers a loss of heat equivalent to the work done against the atmosphere, if the volume increases; or, the system gains an amount of heat equivalent to the work done on the system by the atmosphere, if the volume decreases. Under these conditions, the reaction is said to take place at constant pressure. The difference between constant volume and constant pressure conditions is, that under the former, the heat equivalent of the work corresponding to any change in volume which may occur, is not considered as having any effect upon the energy of the system; whereas, under the latter, due account is taken of the change in energy resulting from change in volume. Suppose that in a reaction, 1 mol of gas is formed. Under standard conditions of temperature and pressure, the volume of the system will be increased by 22.4 liters.

The formation of gas involves the performance of work against the atmosphere, this work being done at the expense of the heat energy of the system. To calculate the heat equivalent of this work, let us imagine the gas enclosed in a cylinder, fitted with a piston whose area is 1 square centimeter. The normal pressure of the atmosphere on the piston is 76 cm. of mercury, or 1033.3 grams per square centimeter. If the increase in the volume of the gas is 22.4 liters, the piston will be raised through 22,400 cm., and the work done will be $1033.3 \times 22{,}400$ gram-centimeters. The heat equivalent of this change in volume will be $(1033.3 \times 22{,}400) \div 42{,}600 = 542.3$ calories, or 0.5423 large calories. There-

fore, this amount of heat must be added to the heat of the reaction. It should be observed that this correction is independent of the actual value of the pressure upon the system. Thus, if the pressure is increased n times, the volume of the gas will be reduced to $1/n$ of its former value, and the work done will involve moving the piston through $1/n$ of the distance against an n-fold pressure, which is plainly equivalent to the former amount of work. While the correction is independent of the pressure, it is not independent of the temperature. The familiar equation, $pv = RT$, shows us that the work done by a gas is directly proportional to its absolute temperature. Thus, if a gas is evolved at 273°, it will occupy double the volume it would occupy at 0°, and the work done at 273° will involve moving the piston through twice the distance that it would have to be moved at 0°. Theoretically, a gas evolved at the absolute zero would occupy no volume, and hence no work would be done. Introducing the correction for temperature, we see that

$$\frac{542.3}{273} \times T = 1.986\ T \text{ cal.},$$

must be added to the heat of the reaction, where T is the absolute temperature at which the change in volume occurs. For all ordinary purposes, it is sufficiently accurate to take $2\ T$ calories as the correction. Thus, suppose n mols of gas to be formed in a reaction at 17° C.: the amount of heat absorbed will be

$$n \times 2\ (273 + 17) = 580\,n \text{ cal.}$$

Under constant pressure conditions, the symbols, in addition to their usual significance, represent the energy, plus or minus the term, $2\ T$ per mol, the positive sign being used if gas is absorbed, while a negative sign is used if gas is set free. The constant volume condition is a condition in which no account is taken of the external work, even if a change in volume does occur during the reaction, while the constant pressure condition is one in which the external work is taken into consideration. It is apparent therefore, that the relation of the heat energy of a reaction at constant volume, Q_v, to the heat energy at constant pressure, Q_p, can be represented by the equation,

$$Q_p = Q_v - 2\,nT \text{ cal.}, \qquad (15)$$

where n denotes the number of mols of gas formed in excess of those initially present. This equation is of great importance in connection with the determination of heats of combustion in the bomb-calorimeter, in which the reactions necessarily take place under constant volume conditions. Since it is customary to state heats of reaction under constant pressure conditions, the foregoing equation makes it possible to convert heats of combustion, determined under constant volume conditions, into heats of combustion under constant pressure conditions. For example, the combustion of methane takes place in accordance with the equation,

$$(CH_4) + 2\,(O_2) = (CO_2) + 2\,H_2O + 210{,}200 \text{ cal.}$$

It is apparent that the reaction is accompanied by a decrease in volume corresponding to 2 mols of gas; therefore, at 18° C. the correction will be,

$$Q_p = 210{,}200 - 2\,[-2\,(273 + 18)],$$

or

$$Q_p = 211{,}364 \text{ cal.}$$

The volume occupied by solids or liquids is so small as to be negligible, and does not enter into these calculations.

Variation of Specific Heat with Temperature. In a previous chapter (p. 52), it has been shown that the value of the molecular specific heat of a monatomic gas, at constant pressure, is 5.0. According to the kinetic theory of gases, the heat capacity, at constant pressure, of any monatomic gas not only should be constant, but also should be independent of the temperature. This theoretical requirement has been fully confirmed by experiments carried out at temperatures ranging from −80° to 200°. The kinetic theory also indicates that the molal heat capacity of gases, containing more than one atom per molecule, should increase with the molecular complexity of the gas, and also with the temperature. Among the earliest investigators in this field was Le Chatelier,* who showed that the variation of the molecular specific heat of polyatomic gases with temperature could be expressed by the formula,

$$C_p = 6.5 + \alpha T, \tag{16}$$

in which the value of the constant, α, increases with the complexity of the molecule. It was subsequently shown by Nernst,†

* Zeit. phys. Chem., 1, 546 (1887).

† Göttinger Nachrichten, 1, 1906.

that the equation of Le Chatelier does not hold at high temperatures, and he proposed a modified expression of the form,

$$C_p = 3.5 + 1.5\,n + \alpha T, \tag{17}$$

where n denotes the number of atoms in the molecule.

After testing a large number of empirical formulas which have been proposed from time to time, to express the variation of the molal heat capacity of gases with temperature, Lewis and Randall* have selected the following as the most trustworthy: —

For N_2, O_2, CO, NO, HCl, HBr, and HI,

$$C_p = 6.50 + 0.0010\,T: \tag{18}$$

For H_2,

$$C_p = 6.50 + 0.0009\,T: \tag{19}$$

For Cl_2, Br_2, and I_2,

$$C_p = 6.5 + 0.004\,T: \tag{20}$$

For H_2O and H_2S,

$$C_p = 8.81 - 0.0019\,T + 0.00000222\,T^2: \tag{21}$$

For CO_2 and SO_2,

$$C_p = 7.0 + 0.0071\,T - 0.00000186\,T^2: \tag{22}$$

For NH_3,

$$C_p = 7.5 + 0.0042\,T. \tag{23}$$

The use of these equations may be illustrated by calculating the quantity of heat required to raise the temperature of one mol of carbon dioxide from 50° to 100°. To calculate the quantity of heat absorbed, it is necessary to integrate the equation, $Q = C_p dT$, between the desired temperature limits, making use of equation (22) to determine the value of C_p, as follows:

$$\begin{aligned} Q &= \int_{323°}^{373°} (7.0 + 0.0071\,T - 0.00000186\,T^2)\,dT, \\ &= 7.0\,(373 - 323) + \frac{0.0071}{2}\,(373^2 - 323^2) \\ &\qquad - \frac{0.00000186}{3}\,(373^3 - 323^3) \\ &= 350 + 123.54 - 11.28 = 462.26 \text{ cal.} \end{aligned}$$

It will be observed that all of the foregoing formulas are derived for constant pressure conditions. They may readily be

* Jour. Am. Chem. Soc., 34, 1128 (1912).

transformed, however, so as to apply equally well to constant volume conditions, by subtracting 2 calories from the first term of each equation. Thus, equation (18) may be written as follows:

$$C_v = 4.50 + 0.0010\ T, \qquad (24)$$

which will give the molal heat capacity of N_2, O_2, CO, NO, HCl, HBr, and HI at constant volume, since the molal heat capacities of gases at constant volume are known to be approximately 2 calories per degree less than the corresponding values at constant pressure.

Similar expressions for the heat capacity of solids in terms of temperature have already been briefly discussed in an earlier chapter (p. 117).

Up to the present time no satisfactory formulas have been derived to express the relation of the thermal capacities of liquids to temperature.

Variation of Heat of Reaction with Temperature. If a chemical reaction be allowed to take place, first at the temperature t_1, and then at the temperature t_2, the amounts of heat developed in the two cases will be found to be quite different. Let us assume that the initial state of the system is represented by the point A, in the diagram, Fig. 103, and that the final state is represented

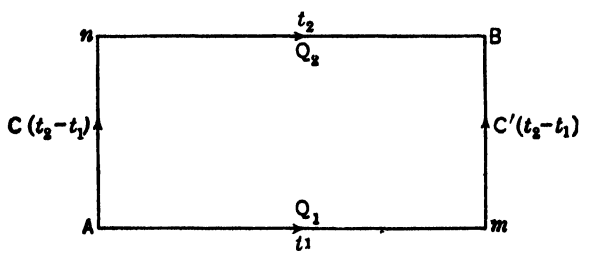

Fig. 103

by the point B. It is evident that we can pass from A to B by two independent paths, namely AnB and AmB. According to the first law of thermodynamics, the net absorption, or evolution, of heat along AnB must be the same as that along AmB, since the system starts from the point A and ends, in both cases, at the same point B, without undergoing any change in volume.

Let Q_1 and Q_2 represent the quantities of heat evolved at the temperatures, t_1 and t_2, respectively. Let us imagine that the

reaction takes place at the temperature t_1, Q_1 units of heat being evolved; and then let the products of the reaction be heated to the temperature t_2. If c' represents the total thermal capacity of the products of the reaction, then the quantity of heat necessary to produce this rise in temperature will be $c'(t_2 - t_1)$. Now, let us imagine the reacting substances, at the temperature t_1, to be heated to the temperature t_2, and then allowed to react, with the evolution of Q_2 units of heat. The heat necessary to produce this rise in temperature in the reacting substances is $c(t_2 - t_1)$, where c is the total thermal capacity of the original substances. Having started with the same substances at the same initial temperature, and having obtained the same products at the same final temperature, we have, according to the first law of thermodynamics,

$$Q_1 - c'(t_2 - t_1) = Q_2 - c(t_2 - t_1),$$

or

$$\frac{Q_2 - Q_1}{t_2 - t_1} = c - c',$$

and, where the change in temperature is very small, we may write,

$$\frac{\Delta Q}{\Delta t} = c - c'. \tag{25}$$

If c' is greater than c then the sign of $\frac{\Delta Q}{\Delta t}$ will be negative, or, in other words, an increase in temperature will cause a decrease in the heat of reaction. On the other hand, if c is greater than c', $\frac{\Delta Q}{\Delta t}$ will be positive and the heat of reaction will increase with the temperature.

EXAMPLE. The reaction between hydrogen and oxygen, at 18° C., is represented by the following equation:

$$2(H_2) + (O_2) = 2H_2O + 1367.1 \text{ K.}$$

Suppose it is required to find how much heat will be evolved when the two gases react at 110° C., the product of the reaction being maintained at this temperature, and the pressure remaining constant. The specific heats, at constant pressure, of the different substances involved, are as follows:*

* It is here assumed that the specific heats of the reacting gases and the reaction product do not vary with the temperature. This of course is not strictly true.

Hydrogen = 3.409; Oxygen = 0.2175; Water (between 18° and 100°) = 1; Water (between 100° and 110°) = 0.5.

The heat of vaporization of water is 537 calories per gram.

For liquid water per degree, we have,

$$\frac{\Delta Q}{\Delta t} = (4 \times 3.409 + 32 \times 0.2175) - (36 \times 1) = -15.404 \text{ cal.},$$

and for $(100° - 18°) = 82°$, we have, $82 \times (-15.404) = -1263$ cal. The heat of formation of liquid water at 100° is, therefore,

$$1367.1 - 12.63 = 1354.47 \text{ K.}$$

When the liquid water is vaporized at 100°, (36×537) calories of this heat are absorbed, or the formation of steam at 100° from hydrogen and oxygen, evolves

$$1354.47 - 193.32 = 1161.15 \text{ K.}$$

For steam, we have,

$$\frac{\Delta Q}{\Delta t} = (4 \times 3.409 + 32 \times 0.2175) - (36 \times 0.5) = 2.596 \text{ cals. per degree,}$$

and for the interval $(110° - 100°) = 10°$,

$$10 \times 2.596 = 25.96 \text{ cal.}$$

Or, for the total heat evolved, we have

$$1161.15 + 0.2596 = 1161.41 \text{ K.}$$

Heat of Combustion. The heat evolved during the complete oxidation of unit mass of a substance is termed its *heat of combustion*. The unit of mass commonly chosen in all physico-chemical calculations is the mol. An enormous amount of experimental work has been done on the determination of the heats of combustion of a large number of chemical compounds by Thomsen,* Berthelot,† Langbein‡ Richards§ and others. The accompanying table gives the heats of combustion of several organic compounds recently determined with extreme accuracy by Richards and Davis.

* Thermochemische Untersuchungen, 4 Vols.

† Essai de Mecanique Chimique, Thermochimie, Donées et Lois Numeriques.

‡ Jour. prakt. Chem., 1885 to 1895.

§ Richards and Barry, Jour. Am. Chem. Soc., 37, 993 (1915); Richards and Davis, ibid., 42, 1599 (1920).

HEATS OF COMBUSTION AT CONSTANT VOLUME

Substance	Heat of Combustion per Mol
Sucrose	1,349,400 cal.
Benzoic acid	771,550
Naphthalene	1,231,600
Benzene	781,850
Toluene	935,230
Tertiary butyl benzene	1,399,800
Cyclohexanol	889,300
Di-isoamyl	1,612,600
Methyl alcohol	170,610
Ethyl alcohol	327,040
Propyl alcohol	485,800
Butyl alcohol	638,330
Isobutyl alcohol	637,140

It has been observed that the average increase in the molal heat of combustion, in any ascending homologous series of hydrocarbons, is 153,500 calories for each CH_2 group added. It has recently been pointed out by Thornton,* that the molal heat of combustion of any saturated hydrocarbon is approximately 52,700 calories for each atomic weight of oxygen required to burn it. For example, the complete combustion of methane may be represented by the equation,

$$(CH_4) + 2\,(O_2) = (CO_2) + 2\,H_2O;$$

since four atomic weights of oxygen are required to burn one mol of methane, it follows, according to Thornton's rule, that the heat of combustion of the latter must be, $4 \times 52{,}700 = 210{,}800$ calories, a value which is in exact agreement with that obtained by direct experiment.

A number of other interesting relations between heats of combustion of compounds and their differences in composition have been discovered, but these cannot be taken up at this time. It has also been pointed out, that the heat of combustion of organic compounds is conditioned not only by their composition, but also by their molecular constitution.†

Some exceedingly interesting and important results have been

* Phil. Mag., 33, 196 (1917).

† Redgrove, Chem. News, 116, 37 (1917); Swietoslawski, Jour. Am. Chem. Soc., 42, 1312 (1920).

obtained with the different allotropic forms of the elements. For example, when equal masses of the three common allotropic forms of carbon are burned successively in oxygen, the amounts of heat evolved are found to be quite different, as is shown by the following energy equations:

$$\begin{aligned} &[C] \text{ diamond} && + 2\,(O) = (CO_2) + 94.3 \text{ Cal.} \\ &[C] \text{ graphite} && + 2\,(O) = (CO_2) + 94.8 \text{ Cal.} \\ &[C] \text{ amorphous} && + 2\,(O) = (CO_2) + 97.65 \text{ Cal.} \end{aligned}$$

It is apparent, that amorphous carbon contains the greatest amount of energy of any one of the three allotropic modifications, and therefore, if this form of carbon were to undergo transformation into the diamond, the reaction would be accompanied by the evolution of $(97.65 - 94.3) = 3.35$ Cal. In like manner, the allotropic forms of both sulphur and phosphorus have different heats of combustion. The following equations express the differences in intrinsic energy between the allotropic forms of the two elements:

$$\text{S (monoclinic)} = \text{S (rhombic)} + 2.3 \text{ Cal.}$$
$$\text{P (white)} = \text{P (red)} + 3.71 \text{ Cal.}$$

When the same substance is burned in oxygen, and then in ozone, it is found, that more heat is evolved in ozone than in oxygen. The energy equation expressing the change of ozone into oxygen may be written thus,

$$(O_3) = 1\tfrac{1}{2}\,(O_2) + 36.2 \text{ Cal.}$$

All of the above facts illustrate the general principle, that larger amounts of intrinsic energy are associated with unstable than with stable forms.

Thermoneutrality of Salt Solutions. In addition to the law of constant heat summation, Hess discovered two other important laws of thermochemistry, viz., the law of thermoneutrality of salt solutions, and the law governing the neutralization of acids by bases.* When two dilute salt solutions are mixed there is neither evolution nor absorption of heat. Thus when dilute solutions of sodium nitrate and potassium chloride are mixed, there is no thermal effect. The energy equation may be written as follows: —

$$NaNO_3, \text{ aq.} + KCl, \text{ aq.} = NaCl, \text{ aq.} + KNO_3, \text{ aq.} + 0 \text{ Cal.}$$

* Pogg. Ann., 50, 385 (1840).

According to this equation, a double decomposition has taken place, and we should naturally expect an evolution, or an absorption, of heat. While Hess could not account for the absence of any thermal effect, he recognized the fact as quite general, and formulated the law of the thermoneutrality of salt solutions, as follows: — *The metathesis of neutral salts in dilute solutions takes place with neither evolution nor absorption of heat.*

The explanation of the phenomenon of thermoneutrality was furnished by the theory of electrolytic dissociation. When the above equation is written in the ionic form, it becomes

$$Na^{\cdot} + NO_3' + K^{\cdot} + Cl' = Na^{\cdot} + Cl' + K^{\cdot} + NO_3'.$$

From this it is apparent, that the same ions exist on both sides of the equation, and in reality no reaction takes place.

There are numerous exceptions to the law of thermoneutrality, but these also can be satisfactorily accounted for by means of the theory of electrolytic dissociation. All of those salts, the behavior of which in dilute solution is contrary to the law, are found to be only partially ionized, and, therefore, when their solutions are mixed, a chemical reaction actually occurs. The exceptions must be considered as furnishing additional evidence in favor of the theory of electrolytic dissociation.

Heat of Neutralization. Hess also discovered,* that when dilute solutions of equivalent quantities of strong acids and strong bases are mixed, practically the same amount of heat is evolved in each case. The following energy equations may be considered as typical examples of such neutralizations:

$$HCl, aq. + NaOH, aq. = NaCl, aq. + H_2O + 13.68\,Cal.,$$
$$HNO_3, aq. + NaOH, aq. = NaNO_3\,aq. + H_2O + 13.69\,Cal.,$$
$$HCl, aq. + KOH, aq. = KCl, aq. + H_2O + 13.93\,Cal.,$$
$$HNO_3, aq. + KOH, aq. = KNO_3, aq. + H_2O + 13.87\,Cal.,$$
$$HCl, aq. + LiOH, aq. = LiCl, aq. + H_2O + 13.70\,Cal.$$

Here again, it would be difficult to explain the phenomenon without the theory of electrolytic dissociation. By means of this theory, however, the explanation is both simple and satisfactory. If MOH and HA represent any strong base and any strong acid, respectively, then when equivalent amounts of these are dissolved

* Loc. cit.

in water, each solution being largely diluted to the same volume, the reaction may be written thus:

$$M^{\cdot} + OH' + H^{\cdot} + A' = M^{\cdot} + A' + H_2O + 13.8\ \text{Cal.}$$

Disregarding the ions which occur on both sides of the equality sign, we have

$$OH' + H^{\cdot} = H_2O + 13.8\ \text{Cal.}$$

It thus appears, that the neutralization of a strong acid by a strong base in dilute solution, consists solely in the combination of hydrogen and hydroxyl ions to form undissociated water. The heat of this ionic reaction is 13.8 large calories. The heat of formation of water from its ions, must not be confused with the heat of formation of water from its elements.

When weak acids, or weak bases are neutralized by strong bases, or strong acids, or when weak acids are neutralized by weak bases, the heat of neutralization may differ widely from 13.8 Cal. This is shown by the following thermochemical equations:

$$H{\cdot}COOH, aq. + NaOH, aq. = H{\cdot}COONa, aq. + H_2O + 13.40\ \text{Cal.},$$

$$CHCl_2{\cdot}COOH, aq. + NaOH, aq. = CHCl_2{\cdot}COONa, aq. + H_2O + 14.83\ \text{Cal.},$$

$$H{\cdot}COOH, aq. + NH_4OH, aq. = H{\cdot}COONH_4, aq. + H_2O + 11.90\ \text{Cal.},$$

$$HCN, aq. + NaOH, aq. = NaCN, aq. + H_2O + 2.90\ \text{Cal.}$$

As will be seen, the heat of neutralization may be either greater, or less, than 13.8 Cal. The exceptions to the rule, that the heat of neutralization of an acid by a base is constant, are readily explained by the theory of electrolytic dissociation. Suppose a weak acid to be neutralized by a strong base. According to the dissociation theory, the acid is only slightly dissociated, and therefore, yields a comparatively small number of hydrogen ions to the solution. The base on the other hand, is completely dissociated into hydroxyl and metallic ions. Therefore, as many hydroxyl ions disappear as there are free hydrogen ions with which they can combine, to form water. When the equilibrium between the acid and the products of its dissociation has been thus disturbed, it undergoes further dissociation, and the resulting hydrogen ions immediately combine with the free hydroxyl ions of the base.

This process continues, until all of the hydroxyl ions of the base have been neutralized. It is evident that the total thermal effect, in this case, must be equal to the algebraic sum of the heat of dissociation of the weak acid, which may be positive or negative, and the heat of formation of water from its ions. A similar explanation holds for the neutralization of a weak base by a strong acid, or for the neutralization of a weak acid by a weak base.

The approximate value of the heat of dissociation of a weak acid, or a weak base may be estimated, provided its heat neutralization by a strong base, or strong acid is known. For example, in the equation given above,

$$HCN, aq. + NaOH, aq. = NaCN, aq. + H_2O + 2.90 \text{ Cal.},$$

the difference between 2.9 and 13.8, or − 10.9 Cal., represents approximately, the heat of dissociation of hydrocyanic acid. Since the acid is initially slightly dissociated in dilute solution, it is apparent, that in order to obtain the true heat of dissociation, we must add to − 10.9 Cal., the thermal value of the dissociation of that portion of the acid which has already become ionized.

It has been shown by Wörmann,* that the average value of 13.8 kilogram calories per mol of water formed, does not remain constant at temperatures much above, or below, room temperature. The following table contains some of Wörmann's data.

HEATS OF NEUTRALIZATION AT DIFFERENT TEMPERATURES

Temperature	Concentration of Acid and Base	KOH + HCl	NaOH + HCl
0°	0.25	14,707 cal.	14,580 cal.
0	0.10	14,709	14,604
6	0.25	14,473	14,352
6	0.1875	14,463	14,359
6	0.125	14,448	14,331
18	0.25	13,937	13,714
18	0.125	13,957	13,693
18	0.05	13,887	13,631
32	0.25	13,155	12,974
32	0.125	13,171	12,922
32	0.05	13,160	12,980

* Ann. der Physik, 18, 775 (1905).

Heat of Ionization. Since 13.8 Cal. is the heat of formation of water from its ions, this must also be the thermal equivalent of the energy required to dissociate one mol of water into its ions. It must be remembered that the dissociated molecule of water must be mixed with a very large volume of undissociated water, in order that the dissociation may be permanent. Reference to the table of heats of formation (p. 343), will show that 68.4 Cal. are required to form one mol of water from its elements. Hence, it follows that 68.4 − 13.8 = 54.6 Cal., is the heat of formation of one equivalent of hydrogen and hydroxyl ions. It has been shown that an extremely small amount of energy is necessary to ionize hydrogen when it is dissolved in water. It is evident, therefore, that 54.6 Cal. is a close approximation to the heat of formation of one equivalent of hydroxyl ions.

On the assumption that the heat of ionization of gaseous hydrogen in solution is zero, the values of the other ionic heats of formation may be computed. For example, the heat of formation of KOH, aq. is 116.5 Cal. The heat of formation of potassium ions must be, 116.5 − 54.6 = 61.9 Cal. In like manner, the heat of formation of KCl, aq. is 101.2 Cal.; hence the heat of formation of chlorine ions must be, 101.2 − 61.9 = 39.3 Cal. The accompanying table of ionic heats of formation has been calculated in this manner.

HEAT OF FORMATION OF IONS

Ion.	Heat of Formation.	Ion.	Heat of Formation.
Hydrogen	0.0	Copper (ic)	−15.8
Potassium	61.9	Copper (ous)	−16.0
Sodium	57.5	Mercury (ous)	−19.8
Lithium	62.9	Silver	−25.3
Ammonium	32.8	Lead	0.5
Magnesium	109.0	Tin (ous)	3.3
Calcium	109.0	Chlorine	39.3
Aluminium	121.0	Bromine	28.2
Manganese	50.2	Iodine	13.1
Iron (ous)	22.2	Sulphate	214.4
Iron (ic)	−9.3	Sulphite	151.3
Cobalt	17.0	Nitrous	27.0
Nickel	16.0	Nitric	49.0
Zinc	35.1	Carbonate	161.1
Cadmium	18.4	Hydroxyl	54.6

The Principle of Maximum Work. A fundamental principle of the science of mechanics is, that a system is in stable equilibrium when its potential energy is a minimum. In 1879, Berthelot * suggested that a similar principle applies to chemical systems.

In terms of the kinetic theory, the temperature of a substance is to be regarded as a measure of the kinetic energy of its molecules. The development of heat by a chemical reaction would, therefore, be taken as an indication of a decrease in the potential energy of the system. Berthelot's theorem, known as the *principle of maximum work*, may be stated as follows: — "*Every chemical reaction which proceeds to completion without the intervention of energy from an external source, tends to produce that substance, or system of substances, which evolves the maximum amount of heat.*" The table of heats of formation (p. 282) illustrates the general truth of this principle, but as will be seen, the theorem precludes the possibility of spontaneous endothermic reactions. Thus, for example, the formation of acetylene from its elements at the temperature of the electric arc is a well-known endothermic reaction, but according to the principle of maximum work, it would not take place spontaneously. Another serious objection to Berthelot's principle is, that according to it, all chemical reactions should proceed to completion, the reaction taking place in such a way as to evolve the greatest amount of heat. As is well known, many reactions, and theoretically all reactions, are never complete, but proceed until a condition of equilibrium is reached. The principle of maximum work, therefore, denies the existence of equilibria in chemical reactions. Many attempts have been made to "explain away" these defects, but none of them have been successful. In referring to the generalization, Le Chatelier terms it "a very interesting approximation toward a strictly valid generalization."

The Theorem of Le Chatelier. As a result of his attempts to modify the principle of maximum work and render it generally applicable, Le Chatelier was led to the discovery of a rigorous law of wide-reaching usefulness. His generalization may be stated as follows: — *Any alteration in the factors which determine an equilibrium, causes the equilibrium to become displaced in such a way as to oppose, as far as possible, the effect of the alteration.* If the temperature of a system which is in equilibrium be raised, or

* Essai de Mecanique Chimique.

lowered, the resulting displacement of the equilibrium is accompanied by such absorption or evolution of heat, as will tend to maintain the temperature constant. An interesting illustration of the behavior of a system when one of the factors controlling the equilibrium is varied, is afforded by the system,

$$2\,NO_2 \rightleftarrows N_2O_4.$$

The reaction proceeds in the direction indicated by the upper arrow, with the evolution of 12.6 Cal. Increase of temperature favors the reaction which is accompanied by an absorption of heat, which in this case, is the reaction indicated by the lower arrow. Hence as the temperature rises, the percentage of NO_2 increases at the expense of N_2O_4. This fact can be demonstrated by the following experiment: Some liquefied N_2O_4 is placed in each of three long glass tubes, which are sealed at one end. When enough N_2O_4 has vaporized to displace the air, the open ends of the tubes are sealed. Changes in the equilibrium, caused by varying the temperature, can be followed by noting the changes in the color of the mixture. The gas, N_2O_4 is an almost colorless substance, while NO_2 is reddish brown. At ordinary temperatures the contents of the tubes will be brown in color. One tube is set aside as a standard of comparison, while the temperature of the second is lowered by surrounding it with a freezing mixture. As the temperature falls, the brown color of the contents of the tube becomes much lighter, showing an increased formation of N_2O_4. The third tube is heated, by immersing it in a beaker of boiling water. As the temperature rises, the contents of the tube becomes much darker in color, indicating an increase in the amount of NO_2 in the mixture.

Another example is afforded by the equilibrium between ozone and oxygen, represented by the equation,

$$2\,O_3 \rightleftarrows 3\,O_2.$$

The reaction indicated by the upper arrow is exothermic. Increase of temperature causes a displacement of the equilibrium in the direction of the lower arrow, since under these conditions heat is absorbed. Thus, as the temperature rises, ozone becomes increasingly stable. Nernst has calculated that at 6000° C., the temperature of the photosphere of the sun, 10 per cent of the

above equilibrium mixture would be ozone. Other applications of the theorem of Le Chatelier will be given in subsequent chapters.

REFERENCE

Thermochemistry. Thomsen. Translated by Burke.

PROBLEMS

1. From the following data calculate the heat of formation of HNO_2 aq. —

$[NH_4NO_3] = (N_2) + 2\,H_2O + 71.77$ Cal.,
$2\,(H_2) + (O_2) = 2\,H_2O + 136.72$ Cal.,
$(N_2) + 3\,(H_2) + aq. = 2\,NH_3\,aq. + 40.64$ Cal.,
$NH_3\,aq. + HNO_2\,aq. = NH_4NO_2\,aq. + 9.110$ Cal.,
$[NH_4NO_3] + aq. = NH_4NO_2\,aq. - 4.75$ Cal.

Ans. $(H) + (N) + (O_2) + aq. = HNO_2\,aq. + 30.77$ Cal.

2. By the combustion at constant pressure of 2 grams of hydrogen with oxygen to form liquid water at 17° C., 68.36 Cal. are evolved. What is the heat evolution at constant volume? *Ans.* 67.49 Cal.

3. The heats of solution of Na_2SO_4, $Na_2SO_4.H_2O$, and $Na_2SO_4.10\,H_2O$ are 0.46, −1.9 and −18.76 Cal. respectively. What are the heats of hydration of Na_2SO_4; (a) to monohydrate, (b) to decahydrate?

Ans. (a) 2.36 Cal., (b) 19.22 Cal.

4. The heats of neutralization of NaOH and NH_4OH by HCl are 13.68 and 12.27 Cal. respectively. What is the heat of ionization of NH_4OH, if it is assumed to be practically undissociated? *Ans.* − 1.41 Cal.

5. From some of the following energy equations: —

$[C] + (O_2) = (CO_2) + 96.96$ Cal.,
$2\,(H_2) + (O_2) = 2\,H_2O + 136.72$ Cal.,
$2\,C_6H_6 + 15\,(O_2) = 12\,(CO_2) + 6\,H_2O + 1598.7$ Cal.,
$2\,(C_2H_2) + 5\,(O_2) = 4\,(CO_2) + 2\,H_2O + 620.1$ Cal.,

all at 17° C. and constant pressure, calculate the heat evolved at 17° C. in the reaction

$$3\,(C_2H_2) = C_6H_6,$$

(a) at constant pressure, and (b) at constant volume.

Ans. (a) 130.8 Cal., (b) 129.07 Cal.

6. Calculate the heat of formation of sulphur trioxide from the following energy equations: —

$[PbO] + [S] + 3\,(O) = [PbSO_4] + 1655$ K.
$[PbO] + H_2SO_4.5\,H_2O = [PbSO_4] + 6\,H_2O + 233$ K.
$[S] + 3\,(O) + 6\,H_2O = H_2SO_4.5\,H_2O + 1422$ K.
$[SO_3] + 6\,H_2O = H_2SO_4.5\,H_2O + 411$ K.
Ans. $[S] + 3\,(O) = [SO_3] + 1011$ K.

7. What is the heat of formation of a very dilute solution of calcium chloride? (See table on p. 358.) *Ans.* 187.6 Cal.

8. Thomsen has shown that the heat of solution of 1 mol of H_2SO_4 in n mols of water can be calculated by the formula:

$$H_s = \frac{17860\,n}{n + 1.798}.$$

Calculate the heat of solution of 1 mol of H_2SO_4 in (a) 5 mols of water and, (b) in 10 mols of water. How many calories are evolved when 10 mols of water are added to a solution containing 1 mol of acid in 10 mols of water?

9. From the preceding formula, calculate the differential heat of dilution for a mixture containing 1 mol of H_2SO_4 and 5 mols of water.

10. The specific heats of the following solutions, $NaOH + 100\,H_2O$, $HCl + 100\,H_2O$, and $NaCl + 201\,H_2O$, are 0.968, 0.964 and 0.978 respectively. The heat of neutralization of first two solutions at 10° is 14253 calories. Calculate the heat of neutralization at 20°.

11. Calculate the quantity of heat required to raise the temperature of 1 mol of steam, at constant pressure, from 100° to 200°.

12. Calculate the number of calories required to raise the temperature of 60 grams of nitric oxide, at constant volume, from 100° to 150°.

13. The heat of combustion of ethyl alcohol is 341800 cals., and the heats of formation of carbon dioxide and water are 96960 cals., and 68369 cals. respectively, all at constant pressure. Calculate the heat of formation of ethyl alcohol.

14. Compute the molal heat of combustion of trimethylmethane by Thornton's rule.

15. The heat of formation of two mols of liquid water from its elements is 137,000 cal. If the molar heat of vaporization of water is 9500 cal., compute the heat of formation of steam from its elements. *Ans.* 118,000 cal.

16. The heat of formation of 2 HBr from its elements is 16,880 cal. at 18° C. The mean specific heats at constant pressure of the two reacting gases and their product are as follows: — $H_2 = 3.409$, $Br_2 = 0.0553$, $HBr = 0.0820$. Calculate the heat of formation of HBr at 150° C.

CHAPTER XII

HOMOGENEOUS EQUILIBRIUM

Historical Introduction. In this, and the two succeeding chapters, the conditions which affect the rate, and the extent of chemical reactions will be considered. When two substances react chemically, it is customary to refer the phenomenon to the existence of an attractive force known as chemical affinity.

Ever since the metaphysical speculations of the Greeks, who endowed the atoms with the instincts of love and hate, the nature of chemical affinity has been under discussion. Newton's discovery of the law of gravitation led him to consider the attraction between atoms, and the attraction between large masses of matter as manifestations of the same force. Although Newton found that chemical attraction does not follow the law of the inverse square, yet his suggestion exerted a profound influence upon the minds of his contemporaries.

Geoffroy and Bergmann arranged chemical substances in the order of their displacing power. Thus, if we have three substances, A, B, and C, and the attraction between A and B is greater than that between A and C, then when B is added to AC, it will completely displace C, as indicated by the following equation:

$$AC + B = AB + C.$$

These investigators overlooked a factor of fundamental importance in conditioning chemical reactivity, namely, the influence of mass. The importance of the relative amounts of the reacting substances in determining the course of a reaction, was first clearly recognized by Wenzel,* in 1777. It remained for Berthollet,† however, to point out the significance of the views advanced by Wenzel. His first paper on this subject was published in 1799, while acting as a scientific adviser to Napoleon on his Egyptian

* Lehre von der chemischen Verwandtschaft der Körper.

† Essai de Statique Chimique.

expedition. Under ordinary conditions, sodium carbonate and calcium chloride react according to the equation,

$$Na_2CO_3 + CaCl_2 = 2\,NaCl + CaCO_3.$$

This reaction was found to proceed nearly to completion. Berthollet observed the deposits of sodium carbonate on the shores of certain saline lakes in Egypt, and pointed out, that this salt is produced by the reversal of the above reaction, the large excess of sodium chloride in solution in the water of the lakes conditioning the course of the reaction.

The German chemist, Rose,* furnished much additional evidence in favor of the effect of mass on chemical reactions. He pointed out, that in nature, the silicates, which are among the most stable compounds known, are undergoing a continual decomposition under the influence of such relatively weak agents as water and carbon dioxide. The relatively strong specific affinities of the atoms of the silicates, are overcome by the preponderating masses of water and carbon dioxide in the atmosphere.

In 1862, an important contribution to our knowledge of the effect of mass on the course of a chemical reaction was made by Berthelot and Péan de St. Gilles.† They investigated the formation of esters from alcohols and acids. The reaction between ethyl alcohol and acetic acid is represented by the equation,

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

Starting with equivalent quantities of alcohol and acid, the reaction proceeds, until about two-thirds of the reacting substances have been converted into ester and water. In like manner, if equivalent quantities of ethyl acetate and water are brought together, the reaction proceeds in the direction indicated by the lower arrow, until about one-third of the original substances have been converted into acid and alcohol. In other words, the reaction is reversible, a condition of equilibrium resulting, when the speeds of the two reactions, indicated by the upper and lower arrows, become equal. If now a fixed amount of acid is taken, say 1 equivalent, and the quantity of alcohol is varied, a corresponding displacement of the equilibrium follows. The following table gives the results, obtained by Berthelot and Péan de St.

* Pogg. Ann., 94, 481 (1855); 95, 96, 284, 426 (1855).

† Ann. Chim. Phys. [3], 65, 385; 66, 5; 68, 225 (1862–1863).

Gilles, for ethyl alcohol and acetic acid. The first and third columns give the number of equivalents of alcohol to 1 equivalent of acetic acid, and the second and fourth columns give the percentage of ester formed.

EQUILIBRIUM IN REACTION BETWEEN ACETIC ACID AND ALCOHOL

Equivalents of Alcohol.	Ester Formed.	Equivalents of Alcohol.	Ester Formed.
0.2	19.3	2.0	82.8
0.5	42.0	4.0	88.2
1.0	66.5	12.0	93.2
1.5	77.9	50.0	100.0

The effect of increasing the mass of alcohol on the course of the reaction is very beautifully shown by the above results.

The Law of Mass Action. While the influence of the relative masses of the reacting substances in conditioning chemical reactions was thus fully established, it was not until 1867 that the law governing the action of mass was accurately formulated.

In that year, Guldberg and Waage,* two Scandinavian investigators, enunciated the law of mass action as follows: — *The rate, or speed, of a chemical reaction is proportional to the active masses of the reacting substances present at that time.* Guldberg and Waage defined the term " active mass," as the molecular concentration of the reacting substances. It is to be carefully noted, that the amount of chemical action is not proportional to the actual masses of the substances present, but rather to the amounts present in unit volume. The law is generally applicable to homogeneous systems; that is, to those systems in which ordinary observation fails to reveal the presence of essentially different parts. The amount of chemical action exerted by a substance, can be determined, either from its effect on the equilibrium, or from its influence on the speed of reaction.

In order to apply the law of mass action practically, it must be formulated mathematically. Let a and b denote the molecular concentrations of the substances initially present in a reversible reaction. According to the law of mass action, the rate at which

* Etudes sur les Affinités Chimiques, Jour. prakt. Chem. [2], 19, 69 (1879).

these substances combine is proportional to the active masses of each constituent, and therefore, to their product, ab. The initial speed of the reaction, at the time t_0, is therefore,

$$\text{Speed}_{t_0} \propto ab, \text{ or } \text{Speed}_{t_0} = k \cdot ab,$$

in which the proportionality factor k, is known as the *velocity constant.* As the reaction proceeds, the molecular concentrations of the original substances steadily diminish, while the molecular concentrations of the products of the reaction steadily increase. Let us assume, that after the interval of time t, x equivalents of the products of the reaction have been formed. The speed of the original reaction will now be,

$$\text{Speed}_t = k\,(a - x)\,(b - x).$$

As the reaction proceeds, the tendency of the products to combine, and reform the original substances, increases. At the time t, when the concentration of the products is x, the speed of the reverse reaction will be,

$$\text{Speed}_t = k_1 \cdot x^2,$$

where k_1 is the velocity constant of the reverse reaction.

We thus have two reactions proceeding in opposite directions; the speed of the direct reaction continuously diminishes while that of the reverse reaction continually increases. It is evident that a point must ultimately be reached at which the speeds of the direct and reverse reactions become equal, and a condition of dynamic equilibrium will be established. Let x_1 represent the value of x, when equilibrium is attained; we have then,

$$\text{Speed}_{\text{direct}} = k\,(a - x_1)\,(b - x_1) = \text{Speed}_{\text{reverse}} = k_1 x_1^2,$$

or

$$\frac{x_1^2}{(a - x_1)\,(b - x_1)} = \frac{k}{k_1} = K, \qquad (1)$$

in which K is known as the *equilibrium constant.* Since the velocity constants, k and k_1, are independent of the concentration, it follows, that the above equation holds for all concentrations. Therefore, if the value of the equilibrium constant of a reaction is known, the equilibrium conditions can be calculated for any concentrations of the reacting substances.

When more than one mol of a substance is involved in a re-

action, each mol must be considered separately in the mass action equation.

Thus, let

$$n_1A_1 + n_2A_2 + \ldots \rightleftarrows n_1'A_1' + n_2'A_2' + \ldots$$

represent any reversible reaction, in which n_1 mols of A_1 and n_2 mols of A_2, react to form n_1' mols of A_1' and n_2' mols of A_2'. When equilibrium is attained, we shall have,

$$k\, c_{A_1}^{n_1} c_{A_2}^{n_2} \ldots = k_1 c_{A_1'}^{n_1'} c_{A_2'}^{n_2'} \ldots$$

or

$$\frac{c_{A_1'}^{n_1'} c_{A_2'}^{n_2'} \ldots}{c_{A_1}^{n_1} c_{A_2}^{n_2} \ldots} = \frac{k}{k_1} = K_c, \tag{2}$$

in which the symbol c is used to denote the active mass, or molecular concentration, of the substances involved in the reaction. This is a perfectly general form of the mass-action equation. Since at any one temperature, concentration and pressure are proportional, we may write equation (2) in the following form:

$$\frac{p_{A_1'}^{n_1'} p_{A_2'}^{n_2'} \ldots}{p_{A_1}^{n_1} p_{A_2}^{n_2} \ldots} = K_p. \tag{3}$$

In the case of gaseous equilibria, this is often a more convenient form of the equation.

The relation between the two equilibrium constants, K_c and K_p, can be easily determined, as follows: — Since $c = \frac{1}{v} = \frac{p}{RT}$ we have, on substituting this value of c in equation (2),

$$\frac{\left(\frac{p_{A_1'}}{RT}\right)^{n_1'} \left(\frac{p_{A_2'}}{RT}\right)^{n_2'} \ldots}{\left(\frac{p_{A_1}}{RT}\right)^{n_1} \left(\frac{p_{A_2}}{RT}\right)^{n_2} \ldots} = RT^{(n_1+n_2)-(n_1'+n_2')} K_p, \tag{4}$$

or, indicating the sum of the initial number of mols by Σn, and the sum of the final number of mols by $\Sigma n'$, we have,

$$K_c = K_p\,(RT)^{\Sigma n - \Sigma n'}. \tag{5}$$

It is evident, therefore, in reactions where the same number of mols occur on both sides of the equality sign, that $K_c = K_p$. Equation (2) is sometimes known as the *reaction isotherm*.

Derivation of the Reaction Isotherm. Let us consider a system, consisting, either of a dilute mixture of gases, or a dilute solution, contained in a closed vessel. Let us assume, that the equilibrium represented by the equation,

$$n_1A_1 + n_2A_2 + \ldots \rightleftarrows n_1'A_1' + n_2'A_2' + \ldots,$$

has been established, and that the partial pressures of A_1, A_2, A_1' and A_2', are p_1, p_2 p_1' and p_2', respectively. We will suppose that n molecules of the reacting substances can be introduced into the reaction chamber, and that at the same time, n' molecules of the products of the reaction can be removed from the reaction chamber, without altering the equilibrium. In other words, for every molecule of a given molecular species which is introduced into the system, an equivalent number of molecules of another molecular species will be displaced, so that the change in the reaction mixture will proceed uniformly, from left to right, without any change occurring in the relative concentrations. Under these conditions, the reaction can be conducted isothermally and reversibly, and the work performed can be calculated thermodynamically. As has been shown in the chapter on thermodynamics, (p. 134) the work required to introduce n_1 mols of A_1 into the reaction chamber against its partial pressure, p_1,* is $n_1RT \ln p_1/p$, where p is the normal external pressure.

In like manner, the corresponding amount of work required to introduce n_2 mols of A_2 into the reaction chamber, will be $n_2RT \ln p_2/p$. Therefore, the total work required to introduce n_1 mols of A_1, and n_2 mols of A_2, into the reaction chamber will be

$$w_1 = -RT\left(n_1 \ln \frac{p_1}{p} + n_2 \ln \frac{p_2}{p}\right), \tag{6}$$

the negative sign indicating work done on the system.

Similarly, the total work performed by the system, when n_1' mols of A_1', and n_2' mols of A_2', are withdrawn from the reaction chamber, will be

$$w_2 = RT\left(n_1' \ln \frac{p_1'}{p} + n_2' \ln \frac{p_2'}{p}\right). \tag{7}$$

The sum of equations (6) and (7) will give the total gain in work resulting from the isothermal transformation of n_1 mols of A_1, and

* It should be remembered that p_1, p_2, etc., may be either gaseous, or osmotic pressures.

n_2 mols of A_2, into n_1' mols of A_1' and n_2' mols of A_2'. Performing this addition, and rearranging terms, we have

$$w_1 + w_2 = W = RT(n_1 \ln p + n_2 \ln p - n_1' \ln p - n_2' \ln p) + RT(n_1' \ln p_1' + n_2' \ln p_2' - n_1 \ln p_1 - n_2 \ln p_2), \quad (8)$$

or

$$W = RT(n_1' \ln p_1' + n_2' \ln p_2' - n_1 \ln p_1 - n_2 \ln p_2) - RT(n_1' \ln p + n_2' \ln p - n_1 \ln p - n_2 \ln p). \quad (9)$$

Equation (9) may be written in the form

$$W = RT \ln \frac{p_1'^{n_1'} p_2'^{n_2'}}{p_1^{n_1} p_2^{n_2}} - RT \ln \frac{p^{n_1'} p^{n_2'}}{p^{n_1} p^{n_2}}. \quad (10)$$

But $\frac{p_1'^{n_1'} p_2'^{n_2'}}{p_1^{n_1} p_2^{n_2}} = K_p$, and if we let P denote all the arbitrary pressure terms, and let $\Sigma n = n_1' + n_2' + \ldots - n_1 - n_2 - \ldots$, equation (10) takes the form,

$$W = RT \ln K_p - RT \Sigma n \ln P. \quad (11)$$

Since the value of the external pressure has nothing to do with the values of the partial pressures of the constituents of the reaction mixture at equilibrium, it may be placed equal to unity. All terms involving ln p will then become zero, and equation (11) may be written in the following form:

$$W = RT \ln K_p, \quad (12)$$

which expresses the law of mass action in its most general form. Since concentration is proportional to pressure, equations (11) and (12) may also be written as follows:

$$W = RT \ln K_c - RT \Sigma n \ln C, \quad (13)$$

and

$$W = RT \ln K_c. \quad (14)$$

A simpler kinetic derivation of the reaction isotherm, has been furnished by van't Hoff. If we assume, that the rate of chemical change is proportional to the number of collisions per unit of time between the molecules of the reacting substances, then in the reaction,

$$n_1 A_1 + n_2 A_2 + \ldots = n_1' A_1' + n_2' A_2' + \ldots,$$

the velocity of the direct change will be $k c_{A_1}^{n_1} c_{A_2}^{n_2} \ldots$, and the velocity of the reverse reaction will be $k_1 c_{A_1'}^{n_1'} c_{A_2'}^{n_2'} \ldots$

At equilibrium, the two velocities will be equal, and therefore,

$$k c_{A_1}^{n_1} c_{A_2}^{n_2} \ldots = k_1 c_{A_1'}^{n_1'} c_{A_2'}^{n_2'} \ldots$$

or

$$\frac{c_{A_1'}^{n_1'} c_{A_2'}^{n_2'} \ldots}{c_{A_1}^{n_1} c_{A_2}^{n_2} \ldots} = \frac{k}{k_1} = K.$$

As a consequence of the assumptions involved in both the thermodynamic and the kinetic proofs of the law of mass action, it follows, that the law is only strictly applicable to very dilute solutions. Notwithstanding this limitation, experimental results indicate that it frequently holds for moderately-concentrated solutions.

Equilibrium in Homogeneous Gaseous Systems.

(a) *Decomposition of Hydriodic Acid.* A typical example of equilibrium in a gaseous system is afforded by the decomposition of hydriodic acid, as represented by the equation,

$$2\,HI \rightleftarrows H_2 + I_2.$$

This reaction has been thoroughly investigated by Hautefeuille, Lemoine and Bodenstein.* The reaction is well adapted for investigation, since it proceeds very slowly at ordinary temperatures, while at the temperature of boiling sulphur, 448° C., equilibrium is established quite rapidly. If the mixture of gases is maintained at 448° C. for some time, and is then cooled quickly, the respective concentrations of the components of the mixture can be determined by the ordinary methods of chemical analysis. Various mixtures of the gases are sealed in glass tubes, and heated for a definite time in the vapor of boiling sulphur. The tubes are then cooled rapidly to the temperature of the room, and after the iodine and hydriodic acid have been removed by absorption in potassium hydroxide, the amount of free hydrogen present in each tube is measured.

Applying the law of mass action to the above equation, we have

$$\frac{c_{H_2} \cdot c_{I_2}}{c^2_{HI}} = K_c.$$

Expressing the analytical results in mols, let a mols of iodine be mixed with b mols of hydrogen, and let $2\,x$ mols of hydriodic acid be formed. Then, when equilibrium is established, $a - x$ will be the amount of iodine vapor, and $b - x$ will be the amount of hydrogen present. The concentrations being directly proportional to the amounts present, we may substitute these values for c_{H_2}, c_{I_2}, and c_{HI} in the mass-action equation. The following expression is thus obtained:

$$\frac{(b - x)\,(a - x)}{4\,x^2} = K_c.$$

* Zeit. Phys., Chem., 22, 1 (1897).

Solving the equation for x, we obtain,

$$2x = \frac{a + b - \sqrt{a^2 + b^2 - ab\,(2 - 16\,K_c)}}{1 - 4\,K_c}.$$

Since, according to Avogadro's hypothesis, equal volumes of all gases contain the same number of molecules, volumes may be substituted for a, b, and x. Bodenstein expressed his results in terms of volumes, reduced to standard conditions of temperature and pressure. On analyzing equilibrium mixtures, Bodenstein found, that at 448° C., $K_c = 0.01984$, and at 350° C., $K_c = 0.01494$. Having determined the value of the equilibrium constant, he made use of this value to calculate the volume of hydriodic acid which should be obtained from known volumes of hydrogen and iodine. A comparison of the calculated and observed values, showed excellent agreement. The following table contains a few of the results obtained by Bodenstein at 448° C.

EQUILIBRIUM IN REACTION BETWEEN HYDROGEN AND IODINE

Hydrogen, b.	Iodine, a.	HI calculated, $2x$.	HI observed, $2x$.
20.57	5.22	10.19	10.22
20.60	14.45	25.54	25.72
15.75	11.90	20 65	20.70
14.47	38.93	27.77	27.64
8.10	2.94	5.64	5.66
8.07	9.27	13.47	13.34

It is of interest to note that a change in pressure does not alter the equilibrium in this gaseous system. Making use of the partial pressures of the components of the gaseous system, instead of the concentrations, we have

$$\frac{p_{H_2} \cdot p_{I_2}}{p^2_{HI}} = K_p.$$

Now let the total pressure on the system be increased to n times its original value; under these conditions the partial pressures are all increased in the same proportion, and we have

$$\frac{np_{H_2} \cdot np_{I_2}}{n^2 p^2_{HI}} = K_p,$$

which will be seen to be equivalent to the original expression, since n cancels out. The equilibrium is thus seen to be independent of the pressure. This is only true for those systems in which a change in volume does not occur.

(*b*) *Dissociation of Phosphorus Pentachloride.* When phosphorus pentachloride is vaporized it dissociates according to the following equation,

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

Applying the law of mass action, we have

$$\frac{c_{PCl_3} \cdot c_{Cl_2}}{c_{PCl_5}} = K_c.$$

Starting with 1 mol of phosphorus pentachloride, which if undissociated would occupy the volume V', under atmospheric pressure, and letting α denote the degree of dissociation, the molecular concentrations at equilibrium will be as follows:

$$c_{PCl_5} = \frac{1-\alpha}{(1+\alpha)V'}, \quad c_{PCl_3} = \frac{\alpha}{(1+\alpha)V'}, \quad \text{and} \quad c_{Cl_2} = \frac{\alpha}{(1+\alpha)V'}.$$

Letting $(1 + \alpha) V' = V$, and substituting in the above equation, we have

$$\frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V} = K_c.$$

At 250° C., phosphorus pentachloride is dissociated to the extent of 80 per cent. Under atmospheric pressure, 1 mol if undissociated will be present in $22.4 \frac{273+250}{273}$ liters $= V'$. Therefore, the final volume will be,

$$V = (1 + 0.8)\left(22.4 \frac{273+250}{273}\right).$$

The value of the equilibrium constant — usually designated in cases of dissociation, the *dissociation constant* — is, therefore,

$$K_c = \frac{(0.8)^2}{(1-0.8)(1+0.8)\left(22.4 \frac{273+250}{273}\right)}$$

Having obtained the value of K_c, the direction and extent of the reaction at 250° C. can be determined, provided the initial molecular concentrations are known. The reaction is accompanied by a change in volume, and therefore, the equilibrium is displaced by a change in pressure. Making use of the partial pressures of the components of the gaseous mixture, we have,

$$\frac{p_2^2}{p_1} = K_p,$$

where p_1 and p_2, are the partial pressures of phosphorus pentachloride and the products of the dissociation, phosphorus trichloride and chlorine, respectively. Let the total pressure be increased n-times, then,

$$K_p = \frac{n^2 p_2^2}{np_1} = \frac{np_2^2}{p_1}.$$

It is apparent from this equation, that the equilibrium is not independent of the pressure, an increase in pressure being accompanied by a diminution of the dissociation. An important point in connection with dissociation, first observed by Deville,* is the effect on the equilibrium of the addition of an excess of one of the products of dissociation. For example, in the equilibrium,

$$PCl_5 \rightleftarrows PCl_3 + Cl_2,$$

an excess of chlorine, or of phosphorus trichloride, drives back the dissociation. If p_1 denotes the partial pressure of phosphorus pentachloride, p_2 that of phosphorus trichloride, and p_3 that of chlorine, then we have,

$$\frac{p_2 \cdot p_3}{p_1} = K_p.$$

Now let an excess of chlorine be added; this will cause the value of p_3 to increase. Since the value of K_p is constant, the value of p_2 must diminish, and that of p_1 must increase. Hence, the addition of an excess of either product of dissociation causes a diminution of the amount of the dissociation.

* Leçons sur la dissociation, Paris (1866).

(c) *Dissociation of Carbon Dioxide.* Carbon dioxide dissociates according to the equation,

$$2\,CO_2 \rightleftarrows 2\,CO + O_2.$$

This is a somewhat more complex gaseous system than either of the foregoing systems. When equilibrium is established, let p_1 be the partial pressure of the carbon dioxide, p_2 the partial pressure of carbon monoxide, and p_3 the partial pressure of oxygen, then we have

$$\frac{p_2^2 \cdot p_3}{p_1^2} = K_p.$$

At 3000° C., and under atmospheric pressure, carbon dioxide is 40 per cent dissociated. The partial pressures of each of the components may be readily calculated as follows:

$$p_1 = \frac{2\,(1 - 0.40)}{2\,(1 - 0.40) + 3 \times 0.40} = 0.50,$$

$$p_2 = \frac{2 \times 0.40}{2\,(1 - 0.40) + 3 \times 0.40} = 0.33,$$

$$p_3 = \frac{0.40}{2\,(1 - 0.40) + 3 \times 0.40} = 0.17.$$

Substituting these values in the above equation, we obtain,

$$K_p = \frac{(0.33)^2 \times 0.17}{(0.50)^2} = 0.074.$$

The dissociation constant for carbon dioxide may have a different value if the equation is written in the form,

$$CO_2 \rightleftarrows CO + \tfrac{1}{2}\,O_2.$$

Applying the law of mass action, we have,

$$K_p = \frac{p_2 \sqrt{p_3}}{p_1}.$$

Substituting the above values of the partial pressures, we obtain,

$$K_p = 0.272.$$

Equilibrium in Liquid Systems. The reaction between an alcohol and an acid, to form an ester and water, may be taken as

an example of equilibrium in a liquid system. In the reaction,

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

let a, b, and c represent the number of mols of alcohol, acid and water respectively, which are present in V liters of the mixture, and let x denote the number of mols of ester and water which have been formed, when the system has reached equilibrium.

The active masses of the components will be,

$$C_{alc.} = \frac{a-x}{V}, \quad C_{acid} = \frac{b-x}{V}; \quad C_{ester} = \frac{x}{V}; \text{ and } C_{water} = \frac{c+x}{V}.$$

Applying the law of mass action, we obtain,

$$\frac{x\,(c+x)}{(a-x)\,(b-x)} = K_c.$$

In this case, the value of the equilibrium constant is independent of the volume. This reaction has been studied, as already mentioned, by Berthelot and Péan de St. Gilles.* They found that when equivalent amounts of alcohol and acid are mixed, the reaction proceeds until two-thirds of the mixture is changed into ester and water. Hence, we find,

$$K_c = \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4.$$

Having determined the value of K_c, it may now be used to calculate the equilibrium conditions for any initial concentrations of the substances involved in the reaction. As an illustration, we will take 1 mol of acetic acid and treat it with varying amounts of alcohol, the initial mixture containing neither of the products of the reaction. The equation takes the form,

$$\frac{x^2}{(a-x)\,(1-x)} = 4.$$

Solving for x, we have,

$$x = \tfrac{2}{3}\,(1 + a - \sqrt{a^2 - a + 1}).$$

A comparison of the observed and calculated values, given in the accompanying table, shows that the agreement is excellent, even in the more concentrated solutions, where we might reasonably expect that the mass law would cease to hold.

* Loc. cit.

EQUILIBRIUM IN THE REACTION BETWEEN ACETIC ACID AND ALCOHOL

Alcohol, a.	Ester (observed), x.	Ester (calculated), x.
0.05	0.05	0.049
0.08	0.078	0.078
0.18	0.171	0.171
0.28	0.226	0.232
0.33	0.293	0.311
0.50	0.414	0.523
0.67	0.519	0.528
1.0	0.665	0.667
1.5	0.819	0.785
2.0	0.858	0.845
2.24	0.876	0.864
8.0	0.966	0.945

Derivation of the Reaction Isochore. The displacement of the equilibrium of a system at constant volume, resulting from a change in temperature, may readily be determined by applying the Gibbs-Helmholtz equation (see p. 184) to the equation of the reaction isotherm. Since at the same temperature, concentrations are proportional to partial pressures, equation (12) may be written in the form,

$$W = RT \ln K_c. \tag{15}$$

Differentiating equation (15), we have

$$dW = RdT \ln K_c + RTd (\ln K_c), \tag{16}$$

which, when combined with the Gibbs-Helmholtz equation, viz.,

$$W + U = T\frac{dW}{dT},$$

gives

$$\frac{d (\ln K_c)}{dT} = \frac{U}{RT^2}. \tag{17}$$

Since the process takes place at constant volume, it follows that the *increase* in total energy, U, may be replaced by Q_v, the heat absorbed when no external work is performed. Therefore equation (17) becomes,

$$\frac{d (\ln K_c)}{dT} = \frac{Q_v}{RT^2}. \tag{18}$$

This expression, which was originally derived by van't Hoff, is commonly known as the equation of the *reaction isochore*. It should be noted that, in the derivation of equation (18), we are dealing with the concentrations, and not with the partial pressures, of the different molecular species involved in the reaction. While it was immaterial in the equation of the reaction isotherm whether we made use of concentrations, or pressures, this is not the case with the reaction isochore, since, at constant volume, the concentration of a substance remains constant while the pressure does not.

In order to derive a similar expression, involving K_p and Q_p, we make use of equation (5), expressing the relation between the two equilibrium constants, viz.,

$$K_c = (RT)^{\Sigma n - \Sigma n'} K_p.$$

On substituting this value of K_c in equation (18), we have

$$\frac{d}{dT}\left[\ln (RT)^{\Sigma n - \Sigma n'} K_p\right] = \frac{Q_v}{RT^2}, \tag{19}$$

which becomes on simplifying,

$$\frac{d}{dT}\left[\ln K_p + \ln (RT)^{\Sigma n - \Sigma n'}\right] = \frac{Q_v}{RT^2},$$

or,

$$\frac{d \ln K_p}{dT} + \frac{\Sigma n - \Sigma n'}{T} = \frac{Q_v}{RT^2}.$$

Therefore,

$$\frac{d (\ln K_p)}{dT} = \frac{Q_v}{RT^2} - \left(\frac{\Sigma n - \Sigma n'}{T}\right),$$

$$= \frac{Q_v - (\Sigma n - \Sigma n')\, RT}{RT^2}. \tag{20}$$

The term $(\Sigma n - \Sigma n')\, RT$, however, is equivalent to the external work nRT; but

$$nRT = Q_v - Q_p;$$

hence, equation (20) becomes,

$$\frac{d (\ln K_p)}{dT} = \frac{Q_p}{RT^2}. \tag{21}$$

Both equations (20) and (21) show that the rate of change of the natural logarithm of the equilibrium constant with temperature is equal to the total heat of reaction, divided by the molar gas constant multiplied by the square of the absolute temperature at which the reaction takes place.

Equations (20) and (21) hold only for displacements of the equilibrium due to infinitely small changes in temperature. In order to render these equations applicable to concrete equilibria, it is necessary to integrate them. The integration of these expressions can only be performed if Q is constant. For small intervals of temperature, Q is practically constant, and for larger intervals, we may take the value of Q which corresponds to the mean of the two temperatures between which the integration is performed. Integrating equations (20) and (21) on this assumption, we obtain,

$$\ln K_{c_2} - \ln K_{c_1} = \frac{Q_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \tag{22}$$

and

$$\ln K_{p_2} - \ln K_{p_1} = \frac{Q_p}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{23}$$

Passing to Briggsian logarithms, and putting $R = 1.99$ calories, equations (22) and (23) become,

$$\log K_{c_2} - \log K_{c_1} = \frac{Q_v}{4.581}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \tag{24}$$

and

$$\log K_{p_2} - \log K_{p_1} = \frac{Q_p}{4.581}\left(\frac{T_2 - T_1}{T_1 T_2}\right). \tag{25}$$

The assumption that Q_v and Q_p, in equations (22) and (23), are independent of the temperature is, in fact, only approximately true, even for relatively small temperature intervals. It has been pointed out by Nernst and others, that the total energy, U, may be expressed in terms of a series involving ascending powers of T. Thus the change in the total energy of a gaseous reaction with the temperature may be expressed by the series,

$$U = U_0 + \alpha T + \beta T^2 + \ldots,$$

in which U_0 is the heat of the reaction in the vicinity of the ab-

solute zero. Introducing this value of U into equation (17) and integrating, we have

$$\ln K_c = \frac{-U_0}{RT} + \frac{\alpha}{R}\ln T + \frac{\beta}{R}T + \ldots + i, \qquad (26)$$

where i is the constant of integration. If the integration be carried out between any two temperatures, T_1 and T_2, the integration constant disappears, and we obtain the expression,

$$\ln K_2 - \ln K_1 = \frac{U_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{\alpha}{R}\ln\frac{T_2}{T_1} + \frac{\beta}{R}(T_2 - T_1). \qquad (27)$$

For further information as to the significance of equation (27), the student must familiarize himself with the Nernst heat theorem. We shall now proceed to show how these important equations may be applied to several typical equilibria.

(a) *Vaporization of Water.* The equilibrium between a liquid and its vapor is conditioned by the pressure of the vapor, this in turn being dependent upon the temperature. In this case we have $K_{p_1} = p_1$, and $K_{p_2} = p_2$. The value of Q_p for water can be calculated from the following data:

$$T_1 = 273°, \qquad p_1 = 4.54 \text{ mm. of mercury},$$
$$T_2 = 273° + 11°.54, \quad p_2 = 10.02 \text{ mm. of mercury}.$$

Substituting in equation (23), we have

$$Q_p = \frac{4.581\ (\log 10.02 - \log 4.54)\ 273 \times 284.5}{284.5 - 273},$$

or

$$Q_p = +\ 10{,}670 \text{ calories}.$$

The value of Q_p obtained by experiment is 10,854 calories.

(b) *Dissociation of Nitrogen Tetroxide.* In the reaction,

$$N_2O_4 \rightleftarrows 2\ NO_2,$$

the following values for the dissociation of N_2O_4 have been obtained:

$$T_1 = 273° + 26°.1, \qquad \alpha_1 = 0.1986,$$
$$T_2 = 273° + 111°.3, \qquad \alpha_2 = 0.9267.$$

If the dissociation takes place under a pressure of 1 atmosphere, then the partial pressures of the component gases will be

$$p_{N_2O_4} = \frac{1-\alpha}{1-\alpha+2\alpha}, \quad \text{and} \quad p_{NO_2} = \frac{2\alpha}{1-\alpha+2\alpha}.$$

The values of K_{p_1} and K_{p_2} are, then, according to the law of mass action as follows:

$$K_{p_1} = \frac{\left(\frac{2\alpha_1}{1+\alpha_1}\right)^2}{\frac{1-\alpha_1}{1+\alpha_1}} = \frac{4\alpha_1^2}{1-\alpha_1^2},$$

and

$$K_{p_2} = \frac{\left(\frac{2\alpha_2}{1+\alpha_2}\right)^2}{\frac{1-\alpha_2}{1+\alpha_2}} = \frac{4\alpha_2^2}{1-\alpha_2^2}.$$

Substituting in equation (23) and solving for Q_p, we obtain

$$+Q_p = \frac{4.581\left[\log\frac{4\times(0.9267)^2}{1-(0.9267)^2} - \log\frac{4\times(0.1986)^2}{1-(0.1986)^2}\right] 299.1 \times 384.3.}{384.3 - 299.1}$$

or,

$Q_p = +$ 12,260 calories per mol of N_2O_4.

In a reaction which is accompanied by no thermal change, $Q_v = Q_p = 0$, and the right-hand side of equations (18) and (21) becomes equal to zero. In other words, in such a reaction a change in temperature does not cause a displacement of the equilibrium.

The reaction,

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COO.C_2H_5 + H_2O,$$

is accompanied by such a small thermal change that it may be considered as zero, and according to the above reasoning, there should be only a very slight displacement of the equilibrium when the temperature is varied. Berthelot found that at 10° C., 65.2 per cent of the alcohol and acid are changed into ester, and at 220° C., 66.5 per cent of the mixture is transformed into ester. As will be seen, an increase of 210° produces hardly any displacement of the equilibrium.

REFERENCES

Chemical Statics and Dynamics. Mellor. Chapters IV and VIII.
Thermodynamics and Chemistry. Nernst. Lectures II to IV incl.
A System of Physical Chemistry. Lewis. Vol. II. Chapters V and XII.
Treatise on Physical Chemistry. Taylor. Vol. I, Chapter VIII.

PROBLEMS

1. When 2.94 mols of iodine and 8.10 mols of hydrogen are heated at constant volume at 444° C. until equilibrium is established, 5.64 mols of hydriodic acid are formed. If we start with 5.30 mols of iodine and 7.94 mols of hydrogen, how much hydriodic acid is present at equilibrium at the same temperature? *Ans.* 9.49 mols.

2. At 2000° C., and under atmospheric pressure, carbon dioxide is 1.80 per cent dissociated according to the equation

$$2\,CO_2 \rightleftarrows 2\,CO + O_2.$$

Calculate the equilibrium constant for the above reaction using partial pressures. *Ans.* 3×10^{-6}

3. What is the equilibrium constant in the preceding problem, if the concentrations are expressed in mols per liter?

4. When 6.63 mols of amylene and 1 mol of acetic acid are mixed, 0.838 mol of ester is formed in the total volume of 894 liters. How much ester will be formed when we start with 4.48 mols of amylene and 1 mol of acetic acid in the volume of 683 liters? *Ans.* 0.8111 mol.

5. If 1 mol of acetic acid and 1 mol of ethyl alcohol are mixed, the reaction

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

proceeds until equilibrium is reached, when $\frac{1}{3}$ mol of ethyl alcohol, $\frac{1}{3}$ mol of acetic acid, $\frac{2}{3}$ mol of ethyl acetate, and $\frac{2}{3}$ mol of water are present. If we start (a) with 1 mol of acid and 2 mols of alcohol; (b) with 1 mol of acid, 1 mol of alcohol, and 1 mol of water; (c) with 1 mol of ester and 3 mols of water, how much ester will be present in each case at equilibrium?

6. In the reaction

$$HCl + \tfrac{1}{4}\,O \rightleftarrows \tfrac{1}{2}\,H_2O + Cl,$$

we find, since $\frac{1}{4}\,O = \frac{1}{2}\,O_2$, for

$$K_p = \frac{\sqrt{p_{H_2O}} \cdot \sqrt{p_{Cl}}}{p_{HCl} \cdot \sqrt[4]{p_o}},$$

the values 3.02 at 386° C. and 2.35 at 419° C. Calculate the heat evolved by the reaction under constant pressure. *Ans.* 6896 cal.

7. Above 150° C. NO_2 begins to dissociate according to the equation

$$NO_2 \rightleftarrows NO + \tfrac{1}{2}\,O_2.$$

At 390° C. the vapor density of NO_2 is 19.57 ($H_2 = 1$), and at 490° C. it is 18.04. Calculate the degree of dissociation according to the above equation at each of these temperatures; the equilibrium constants expressing the concentrations in mols per liter; and the heat of dissociation of NO_2. *Ans.* $\alpha_1 = 0.35$, $\alpha_2 = 0.55$, $K_1 = 2.812 \times 10^{-2}$. $K_2 = 7.17 \times 10^{-2}$. $Q = 9407$ cal.

8. In the reaction

$$2\,SO_3 \rightleftarrows 2\,SO_2 + O_2,$$

the equilibrium constant, K_c, has been found to have the following values at different temperatures:

Temp.	K_c
627°	0.000316
727	0.00354
832	0.0280

Calculate the corresponding values of K_p.

9. From the data of the preceding problem, calculate the values of K_c and K_p at 500°, and also calculate the heat of reaction at this temperature.

CHAPTER XIII

HETEROGENEOUS EQUILIBRIUM

Heterogeneous Systems. We have now to consider equilibria in systems made up of matter in different states of aggregation. Such systems are termed *heterogeneous systems*, as distinguished from those dealt with in the preceding chapter, where the composition is uniform throughout. The physically distinct portions of matter involved in a heterogeneous system are known as *phases*, each phase being homogeneous, and separated from the other phases by definite bounding surfaces. Thus, ice, liquid water and vapor, constitute a physically heterogeneous system. Another heterogeneous system is formed by calcium carbonate and its products of dissociation, calcium oxide and carbon dioxide. The equilibrium between a solid, its saturated solution, and vapor affords an illustration of a still more complex heterogeneous system.

Application of the Law of Mass Action to Heterogeneous Equilibria. It has been shown in the preceding chapter, that the law of mass action may be applied to homogeneous equilibria, provided the molecular condition of the reacting substances is known.

When we attempt to apply the law of mass action to heterogeneous equilibria, especially where solids are involved, the problem presents difficulties. In his investigation of the dissociation of calcium carbonate, according to the equation,

$$[CaCO_3] \rightleftarrows [CaO] + (CO_2),$$

Debray * showed, that just as every liquid has a definite vapor pressure corresponding to a certain temperature, so there is a definite pressure of carbon dioxide over calcium carbonate, at a definite temperature. Furthermore, the pressure was found to be independent of the amount of calcium carbonate present.

* Compt. rend., 64, 603 (1867).

Guldberg and Waage* showed that the law of mass action can be applied to such heterogeneous equilibria, provided that the active masses of the solids present are considered as constant. Nernst confirmed this statement of Guldberg and Waage and showed how it can be reconciled with experimental facts. In a heterogeneous equilibrium involving solids, it is only necessary to consider the gaseous phase, since the active mass of a solid is equivalent to its concentration in the gaseous phase. That is, every solid is to be looked upon as possessing, at a definite temperature, a definite vapor pressure which is entirely independent of the amount of solid present. Such substances as arsenic, antimony, and cadmium are known to have appreciable vapor pressures at relatively low temperatures, and it is quite reasonable to suppose, that every solid substance exerts a definite vapor pressure at a definite temperature, even though we have no method sufficiently refined to measure such minute pressures.

Since the active mass of a solid remains constant so long as any of it is present, the application of the law of mass action to certain heterogeneous equilibria is, in general, simpler than its application to homogeneous systems. The truth of this statement will be evident after a few typical heterogeneous systems have been considered.

(a) *Dissociation of Calcium Carbonate.* In the reaction,

$$[CaCO_3] \rightleftarrows [CaO] + (CO_2),$$

let π_1 and π_2 represent the pressures due to the vapor of calcium carbonate and calcium oxide respectively, and let p denote the pressure of the carbon dioxide. Applying the law of mass action, we obtain,

$$\frac{\pi_2 p}{\pi_1} = K_p.$$

But, since π_1 and π_2 are constant at any one temperature, the equation becomes,

$$p = K_p',$$

or, the equilibrium constant, at any one temperature, is solely dependent upon the pressure of the carbon dioxide evolved. The accompanying table gives the values of the pressure of carbon dioxide corresponding to various temperatures.

* Loc. cit.

DISSOCIATION PRESSURES OF $CaCO_3$

Temperature, Degrees.	Pressure in Millimeters of Mercury.
547	27
610	46
625	56
740	255
745	289
810	678
812	753
865	1333

(b) *Dissociation of Ammonium Hydrosulphide.* When solid ammonium hydrosulphide is heated, it is almost completely dissociated into ammonia and hydrogen sulphide, as shown by the following equation:

$$[NH_4HS] \rightleftarrows (NH_3) + (H_2S).$$

This reaction was investigated by Isambert,* who found that the total gas pressure at 25°.1 C., is equal to 501 mm. of mercury. Since the partial pressures of the ammonia and hydrogen sulphide are necessarily the same, each must be approximately equal to 250.5 mm., the relatively small pressure due to the undissociated vapor of the ammonium hydrosulphide being neglected. Let π be the partial pressure of the vapor of ammonium hydrosulphide, and let p_1 and p_2 be the partial pressures of the ammonia and hydrogen sulphide respectively. Applying the law of mass action, we have

$$\frac{p_1 \cdot p_2}{\pi} = K_p. \tag{1}$$

Since π is constant at any one temperature, equation (1) becomes,

$$p_1 \cdot p_2 = K_p'.$$

According to Dalton's law of partial pressures, we have

$$P = p_1 + p_2 + \pi,$$

where P is the total pressure. Neglecting the relatively small pressure π, we may write,

$$P = p_1 + p_2.$$

* Compt. rend., 93, 595, 730 (1881).

Hence, since $p_1 = p_2$,

$$\frac{P}{2} = p_1 = p_2.$$

Substituting these values in equation (1), we obtain

$$\frac{P^2}{4} = K_p' = \frac{(501)^2}{4} = 62{,}750. \qquad (2)$$

The value of the equilibrium constant may be checked, by observing the effect on the system of the addition of an excess of either one of the products of the dissociation. The accompanying table gives the results of a few of Isambert's experiments.

DISSOCIATION PRESSURES OF NH_4HS

Pressure of Ammonia.	Pressure of Hydrogen Sulphide.	$p_{NH_3} \cdot p_{H_2S} = K_p'$.
208	294	61,152
138	458	63,204
417	146	60,882
453	143	64,779
		Mean 62,504

As will be seen, the mean value of the equilibrium constant agrees well with the value found for equivalent amounts of the products of dissociation.

(c) *Dissociation of Ammonium Carbamate.* The dissociation of ammonium carbamate takes place according to the equation,

$$OC\begin{matrix} ONH_4 \\ NH_2 \end{matrix} \rightleftarrows 2\,(NH_3) + (CO_2).$$

This dissociation has been investigated by Horstmann.* Applying the law of mass action, we have

$$\frac{p_1^2 \cdot p_2}{\pi} = K_p, \qquad (3)$$

where p_1 and p_2 are the partial pressures of ammonia and carbon dioxide respectively, and where π is the partial pressure of ammonium carbamate. Since π is constant, equation (3) becomes

$$p_1^2 p_2 = K_p'.$$

* Lieb. Ann., 187, 48 (1877).

If P denotes the total gaseous pressure, and π is neglected as in the preceding example, we have, since three mols of gas are formed,

$$p_1^2 = \frac{4P^2}{9} \quad \text{and} \quad p_2 = \frac{P}{3}.$$

Substituting these values in equation (3), we have

$$\frac{4P^3}{27} = K_p'. \qquad (4)$$

This equation has also been tested by Isambert,* by adding an excess of ammonia, or carbon dioxide, to the dissociating system. He found that the value of the equilibrium constant remains practically constant. Furthermore, the addition of a foreign gas was shown to be without effect on the dissociation.

(d) *Dissociation of the Hydrates of Copper Sulphate.* Many interesting examples of heterogeneous equilibrium are furnished by hydrated salts. Thus, if crystallized copper sulphate, $CuSO_4 \cdot 5\,H_2O$, be placed in a desiccator, it gradually loses water of crystallization, and ultimately the anhydrous salt alone remains. If a desiccator, provided with a manometer, be placed in a thermostat, it is possible to observe the changes in vapor pressure accompanying the process of dehydration. At the temperature of 50° C., the pressure over completely hydrated copper sulphate is found to remain constant at 47 mm., until the salt has been deprived of two molecules of water, when it drops abruptly to 30 mm., and remains constant until two more molecules of water have been lost. It then drops to 4.4 mm., and remains constant until dehydration is complete.

The successive stages of the dehydration are shown in the accompanying diagram, Fig. 104. The constant pressures observed in the dehydration correspond to the successive equilibria involved. At 50° C., the pentahydrate and the trihydrate are in equilibrium, a pressure of 47 mm. being maintained so long as any of the pentahydrate is present. When all of the pentahydrate has disappeared, then the trihydrate begins to undergo dehydration into the monohydrate. This is a new equilibrium, and the pressure of the aqueous vapor necessarily changes, and remains constant so long as any trihydrate remains. The last stage corresponds to the

* Loc. cit.

equilibrium between the monohydrate and the anhydrous salt. The following equations represent the three successive equilibria:

(1) $CuSO_4 \cdot 5\,H_2O \rightleftarrows CuSO_4 \cdot 3\,H_2O + 2\,H_2O$,
(2) $CuSO_4 \cdot 3\,H_2O \rightleftarrows CuSO_4 \cdot H_2O + 2\,H_2O$,
(3) $CuSO_4 \cdot H_2O \rightleftarrows CuSO_4 + H_2O$.

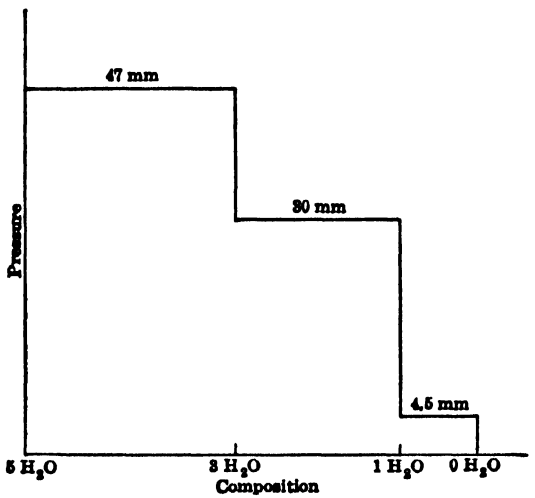

Fig. 104

Applying the law of mass action to the first of the above equilibria, we have

$$\frac{\pi_2 p^2}{\pi_1} = K_p,$$

in which π_1 and π_2 denote the partial pressures due to the hydrates, $CuSO_4 .5\,H_2O$ and $CuSO_4 .3\,H_2O$ respectively, and p denotes the pressure of aqueous vapor. Since π_1 and π_2 are constant, the above expression takes the form,

$$p^2 = K_p'.$$

In a similar manner, it may be shown that the pressure of aqueous vapor in the other equilibria must be constant. It must be clearly understood, that the observed pressure is only definite and fixed when two hydrates are present. If the dehydration were conducted at another temperature than 50° C., the equilibrium

pressure would be different. The vapor pressure curves of the different hydrates are shown diagrammatically in Fig. 105.

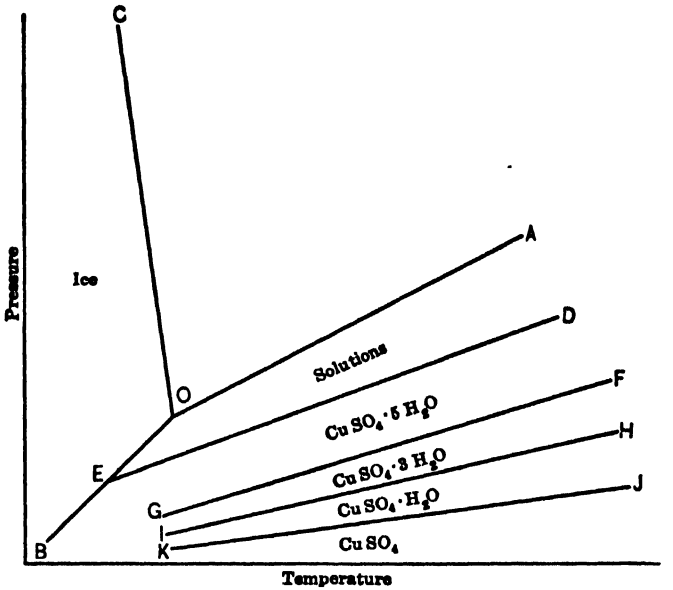

Fig. 105

Heat of Dissociation of Solids. When the products of the dissociation of a solid are gaseous, it has been pointed out by De Forcrand,* that the ratio of the heat of dissociation of 1 mol of solid to the absolute temperature at which the dissociation pressure is equal to 1 atmosphere, is constant. Or, denoting the heat of dissociation by Q, and the absolute temperature by T, De Forcrand's relation may be expressed thus,

$$\frac{Q}{T} = \text{constant} = 33. \qquad (5)$$

Nernst has shown, that the value of the constant in this relation is not independent of the temperature. Thus, the value of the ratio at 100° C., is 29.7, while at 1000° C., it is 37.7. Up to the present time, no expression has been derived, in which the variation of the ratio with the temperature is included.

* Ann. Chim. Phys. [7], 28, 545.

Distribution of a Solute between Two Immiscible Solvents. When an aqueous solution of succinic acid is shaken with ether, the acid distributes itself between the ether and the water in such a way, that the ratio between the two concentrations is always constant. It will be seen, that the distribution of succinic acid between two solvents is analogous to that of a substance between the liquid and gaseous phases (see page 193), and therefore, the laws governing the latter equilibrium should apply equally to the former. Nernst* has shown, that (a) *If the molecular weight of the solute is the same in both solvents, the ratio in which it distributes itself between them is constant, at constant temperature,* or, in other words, Henry's law is applicable; and (b) *If there are several solutes in solution, the distribution of each solute is the same as if it were present alone.* This is clearly Dalton's law of partial pressures. The ratio in which the solute distributes itself between the two solvents is termed the *coefficient of distribution, or partition.* The following table gives the results of three experiments on the distribution of succinic acid between ether and water.

DISTRIBUTION OF SUCCINIC ACID

Concentration in Water.	Concentration in Ether.	Distribution Coefficient.
43.4	7.1	6.1
43.8	7.4	5.9
47.4	7.9	6.0

As will be seen, the distribution coefficient is constant, showing that Henry's law applies. When the molecular weight of a solute is not the same in both solvents, the distribution coefficient is not constant, and conversely, if the distribution coefficient is not constant, we infer that the molecular weights of the solute in the two solvents are not identical.

Let us assume that a solute whose normal molecular weight is A, when shaken with two immiscible solvents, undergoes polymerization in one of them, its molecular weight being A_n. We then have the equilibrium,

$$A_n \rightleftarrows nA:$$

* Zeit. phys. Chem., 8, 110 (1891).

applying the law of mass action, we have

$$\frac{c_A^n}{c_{A_n}} = K_c. \tag{6}$$

If the molecular weight in one solvent is twice the molecular weight in the other, then $n = 2$, and

$$\frac{c_1^2}{c_2} \quad \text{or,} \quad \frac{c_1}{\sqrt{c_2}} = \text{constant.}$$

Thus, Nernst found the following concentrations of benzoic acid when it was shaken with benzene and water.

DISTRIBUTION OF BENZOIC ACID

c_1 (Water).	c_2 (Benzene).	$\frac{c_1}{c_2}$.	$\frac{c_1}{\sqrt{c_2}}$.
0.0150	0.242	0.062	0.0305
0.0195	0.412	0.048	0.0304
0.0289	0.970	0.030	0.0293

As will be seen, the values of the ratio c_1/c_2 steadily decrease, while on the other hand, the values of the ratio $c_1/\sqrt{c_2}$ remain constant. This shows, therefore, that benzoic acid has twice the normal molecular weight in benzene.

The Solution of a Solid in a Non-dissociating Solvent. When a solid is introduced into a non-dissociating solvent, it continues to dissolve, until the solution becomes saturated. A condition of equilibrium then obtains, and the rates of solution and precipitation are the same. This is plainly a case of heterogeneous equilibrium. If c is the concentration of the dissolved substance, and π is the concentration of the undissolved solid, then according to the law of mass action,

$$\frac{c}{\pi} = K_c,$$

or, since π is constant,

$$c = K_c'.$$

Variation of the Constant of Heterogeneous Equilibrium with Temperature. The equation of the reaction isochore,

$$\frac{d\,(\log_e K)}{dT} = \frac{Q}{RT^2},$$

which expresses the variation of the equilibrium constant with temperature, applies equally well to heterogeneous equilibria. The following examples will serve to illustrate its application in such cases.

(a) *Dissociation of Ammonium Hydrosulphide.* In the reaction representing the dissociation of ammonium hydrosulphide,

$$[NH_4HS] \rightleftarrows (NH_3) + (H_2S),$$

let p_1 and p_2 be the partial pressures of ammonia and hydrogen sulphide, and let π be the partial pressure of ammonium hydrosulphide. Then as has been shown,

$$K_p' = \frac{P^2}{4},$$

where P is the total gaseous pressure. From the following data:

$$T_1 = 273° + 9°.5, \qquad P_1 = 175 \text{ mm. of mercury,}$$

and

$$T_2 = 273° + 25°.1, \qquad P_2 = 501 \text{ mm. of mercury,}$$

we have, on applying the reaction isochore equation, and solving for Q_p,

$$Q_p = \frac{4.581\left[\log\left(\frac{501}{2}\right)^2 - \log\left(\frac{175}{2}\right)^2\right]282.5 \times 298.1}{298.1 - 282.5},$$

or,

$$Q_p = 22{,}740 \text{ calories.}$$

This result agrees well with the value, 22,800 calories, found by direct experiment.

(b) *Solution of Succinic Acid.* Concentration and temperature are the factors which determine the equilibrium in a saturated solution. In the equation,

$$\frac{d(\log_e K_c)}{dT} = \frac{Q_v}{RT^2},$$

$K_c = c$, where c is the concentration of succinic acid in a saturated solution. The following experimental data, due to van't Hoff, enables us to calculate the heat of solution of the acid.

$$T_1 = 273°, \; c = 2.88 \text{ grams per 100 grams of water,}$$

and

$$T_2 = 273° + 8°.5, \qquad c = 4.22 \text{ grams per 100 grams of water.}$$

Substituting in the equation of the reaction isochore, and solving for Q_v, we have

$$Q_v = \frac{4.581\ (\log 4.22 - \log 2.88)\ 273 \times 281.5}{281.5 - 273},$$

or

$$Q_v = 6871 \text{ calories.}$$

The value of the heat of solution for 1 mol of succinic acid, as found by direct experiment, is 6700 calories.

The Phase Rule. While it is possible to apply the law of mass action to certain heterogeneous equilibria, there are numerous cases where its application is either difficult, or impossible. In dealing with such heterogeneous systems, we make use of a generalization discovered by J. Willard Gibbs,* late professor of mathematical physics in Yale University. This generalization was first stated by Gibbs in 1874, and is commonly known as the *phase rule.* Before entering upon a discussion of the phase rule, it will be necessary to define a few of the terms employed.

The composition of a system is determined by the number of independent variables, or *components* involved. Thus, in the system — ice, water, and vapor — there is but a single component. In the system,

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

while there are three substances which constitute the equilibrium, only two of these need be considered as components, for the amount of any one constituent is not independent of the amounts of the other two, as the following equations show:

$$CaO + CO_2 = CaCO_3,$$
$$CaCO_3 - CaO = CO_2,$$
$$CaCO_3 - CO_2 = CaO.$$

In general, the components are chosen from the smallest number of independently-variable constituents required to express the composition of each phase entering into the equilibrium, even negative quantities of the components being permissible.

The number of variable factors, — temperature, pressure, and concentration, — of the components which must be arbitrarily fixed in order to define the condition of the system, is known as

* Trans. Connecticut Academy, Vols. II and III, 1875–8.

the *degree of freedom* of the system. For example, a gas has two degrees of freedom, since any two of the three variables, — temperature, pressure, or volume, — must be fixed in order to define it; a liquid and its vapor has only one degree of freedom, since for equilibrium at a certain temperature, there can be but a single pressure; while in a system consisting of a substance in the three states of aggregation, equilibrium can exist only at a single temperature and pressure.

Derivation of the Phase Rule. While the following derivation of the phase rule is neither rigorous nor complete, it serves to illustrate the general method employed by Gibbs in his brilliant and highly mathematical derivation of this important principle governing heterogeneous equilibria.

The degree of freedom, F, of any system, as has already been stated, is the number of variables which must be arbitrarily fixed in order that the system may be completely defined. As will later be apparent, the number of such variables must be equal to the difference between the total number of variables, N_1, of the system, and the number of variables, N_2, which are defined by the system itself; that is, $F = N_1 - N_2$.

Although the composition (or concentration) variables may be numerous, a single temperature and a single pressure must prevail throughout a system which is in a state of stable equilibrium. It follows, therefore, that the temperature and pressure variables together are equal to 2. While the composition of each phase may vary widely, the number of variations within a single phase will always be one less than the number of components, or $(C - 1)$. That this must be true, becomes apparent when we consider a two-component system, and let the composition of one of the components be varied; the variation in the other component can be determined by subtracting the percentage of the first component from 100. In like manner, in a three-component system, the variation in the composition of any one component is derivable from the variation of the other two. It follows, therefore, that the total number of composition variables in all the phases is $P(C - 1)$, while the total number of variables of all kinds must be increased by the two variables, temperature and pressure. Hence we have $N_1 = P(C - 1) + 2$.

In order to evaluate N_2 — the number of variables defined by the system itself — it must be borne in mind that the free energy

of each component in each phase is a function of the three variables, temperature, pressure and composition (or concentration). Just as the temperature throughout all of the parts of a system which is in a state of stable thermal equilibrium must be the same, so also the free energy of each component in every phase of a system which is in equilibrium must be equal. It follows, therefore, that the free energy of the C components in the system will be given by the expression, $N_2 = C\,(P - 1)$.

Substituting the values of N_1 and N_2 in the equation for the degree of freedom, we have

$$F = P\,(C - 1) + 2 - C\,(P - 1),$$

or

$$F = C - P + 2. \qquad (7)$$

This equation summarizes the generalization known as the phase rule.

Equilibrium in the System, Water, Ice, and Vapor. In this system, we may have one, two, or three phases present, according to the conditions. Under ordinary circumstances of temperature and pressure, water and water vapor are in equilibrium. The vapor pressure curve of water is represented by the line OA, in the pressure - temperature diagram (Fig. 106). It is only at points on this curve that water and its vapor are in equilibrium. Thus, if the pressure be reduced below that corresponding to any point on OA, all of the water will be vaporized; if, on the other hand, the pressure be raised above the curve, all of the vapor will ultimately condense to the liquid state. When the temperature is reduced below 0° C., only ice and vapor are present, the curve, OC, representing the equilibrium between these two phases. It is to be observed that the curve, OC, is not continuous with OA. At

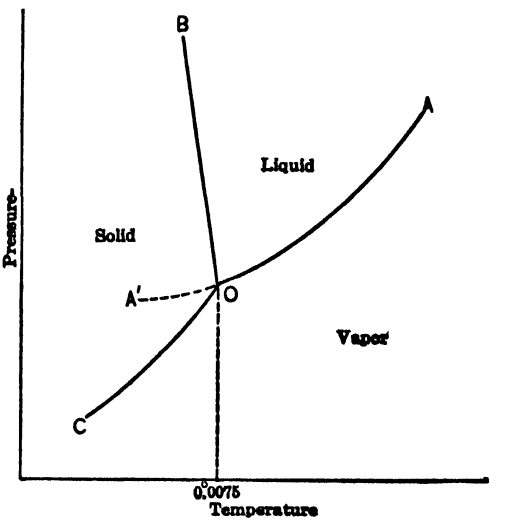

Fig. 106

the point O, where the two curves intersect, ice, water, and water vapor are in equilibrium. At this point, ice and water must have the same vapor pressure, otherwise, distillation of vapor, from the phase having the higher vapor pressure to that with the lower vapor pressure, would occur, and eventually, the phase having the higher vapor pressure would disappear. This result would be in contradiction to the experimentally-determined fact, that both solid and liquid phases are in equilibrium at the point O. The temperature at which ice and water are in equilibrium with their vapor, under atmospheric pressure, is 0° C. Since increase of pressure lowers the freezing-point of water, the point O, representing the equilibrium between ice and water under the pressure of their own vapor, viz., 4.57 mm., must be a little above 0° C. The exact temperature corresponding to the point O has been found to be 0°.0075 C.

The change in the melting-point of ice, due to increasing pressure, is represented by the line OB. This line is inclined toward the vertical axis because the melting-point of ice is lowered by increased pressure. The point O, is called a *triple point*, because there, and there only, three phases are in equilibrium. As is well known, water does not always freeze exactly at 0° C. If the containing vessel is perfectly clean, and care is taken to exclude dust, it is possible to supercool water several degrees below its freezing-point, and measure its vapor pressure.

The dotted curve OA', which is a continuation of OA, represents the vapor pressure of supercooled water. It will be noticed, that (1) there is no break in the vapor-pressure curve, so long as the solid phase does not separate, and (2) the vapor pressure of supercooled water, which is an unstable phase, is greater than that of ice, the stable phase, at that temperature.

We now proceed to apply the phase rule to this system. In the formula, $C - P + 2 = F$, $C = 1$. It is evident that if $P = 3$, then $F = 0$; or, the system has no degree of freedom. We have seen that the triple point O represents such a condition. At this point ice, water, and water vapor are co-existent, and if either one of the variables, temperature or pressure, is altered, one of the phases disappears; in other words, the system has no degree of freedom. Such a system is said to be *non-variant*. If, in the above formula, $P = 2$, then $F = 1$, and the system has one degree of freedom, or is *univariant*. Any point on any one of the curves,

OA, *OB*, or *OC*, represents a univariant system. Take, for example, a point on the curve *OA*. In this case, the temperature may be altered without altering the number of phases in equilibrium. If the temperature is raised, a corresponding increase in vapor pressure follows, and the system will adjust itself to some other point on the curve *OA*. In like manner, the pressure may be altered without causing the disappearance of one of the phases. If, however, the temperature is maintained constant, then a change in the pressure will cause either condensation of water vapor, or vaporization of liquid water. Under these conditions, the system has only one degree of freedom. Again, if $P = 1$, then $F = 2$, and the system is *bivariant*, or has two degrees of freedom. The areas included between the curves in the diagram are examples of bivariant systems. Let us consider the vapor phase. The temperature may be fixed at any desired value within the vapor area *AOC*, and the pressure may be altered along a line parallel to the vertical axis without causing a change in the number of phases, provided

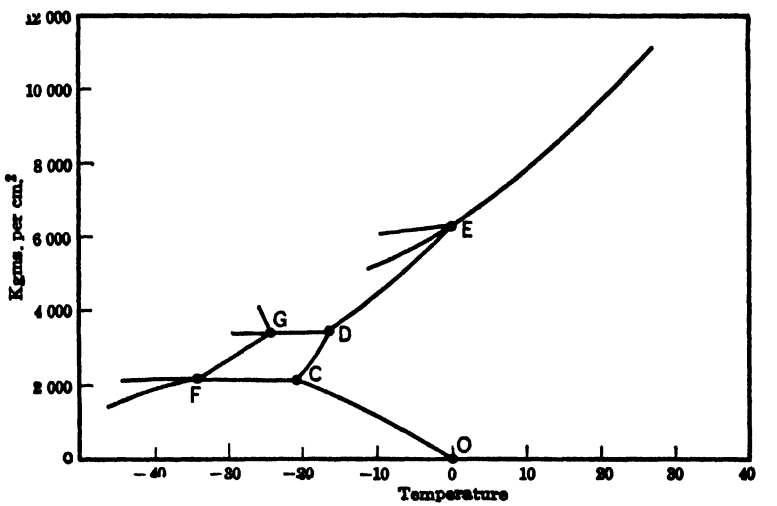

Fig. 107

the curves *OA* and *OC* are not intersected. The lower limit of the sublimation curve *OC*, is theoretically determined by the absolute zero, while the vaporization curve *OA*, terminates at the critical temperature, 364.3°, corresponding to a pressure of 194.6 atmospheres.

Investigations conducted by Tammann,* and Bridgman,† with a view to determining the upper limit of the fusion curve *OB*, have revealed the existence of at least five different crystalline modifications of ice, all of which, with the exception of ordinary ice, are denser than water. These five forms of ice have been designated Ice I (ordinary ice), Ice II, Ice III, Ice V, and Ice VI. Although Tammann's experiments indicate the possibility of the existence of Ice IV, it has not yet been satisfactorily established. The accompanying diagram, Fig. 107, shows the relationships which these different modifications of ice bear to each other. The coördinates of the important points are given below.

Phases	Point	Temp.	Press.
Ice I, liquid and vapor.....	O	+ 0.0075	4.579 mm. Hg.
Ice I, liquid, Ice III.....	C	− 22°	2115 kg. per cm.²
Ice III, liquid, Ice V.....	D	− 17°	3530 "
Ice V, liquid, Ice VI.....	E	+ 0.16°	6380 "
Ice I, Ice II, Ice III.....	F	− 34.7°	2170 "
Ice II, Ice III, Ice V.....	G	− 24.3°	3510 "

The System, Sulphur (Rhombic, Monoclinic), Liquid and Vapor. This system is more complicated than the preceding one-component system, since there are two solid phases, in addition to the liquid and vapor phases. At ordinary temperatures, rhombic sulphur is the stable modification. When this is heated rapidly it melts at 115° C., but if it is maintained in the neighborhood of 100° C., it gradually changes into monoclinic sulphur, which melts at 120° C. Monoclinic sulphur can be kept indefinitely at 100° C. without undergoing change into the rhombic modification, or in other words, it is the stable phase at this temperature. It is evident, therefore, that there must be a temperature above which monoclinic sulphur is the stable form, and below which rhombic sulphur is the stable modification. This temperature at which both rhombic and monoclinic modifications are in equilibrium with each other and with their vapor, is termed the *transition point*. Its value has been determined to be 95°.6 C. The change from one form into the other is relatively slow, so that it is possible to measure the vapor pressure of rhombic sul-

* Ann. der Physik, (4) 2, 1424 (1900).
† Proc. Am. Acad., 47, 411 (1912).

phur up to its melting-point, and that of monoclinic sulphur below its transition point. The vapor pressure of solid sulphur, although very small, has been measured as low as 50° C.

The complete pressure-temperature diagram for sulphur is shown in Fig. 108. At the point *O*, rhombic and monoclinic sul-

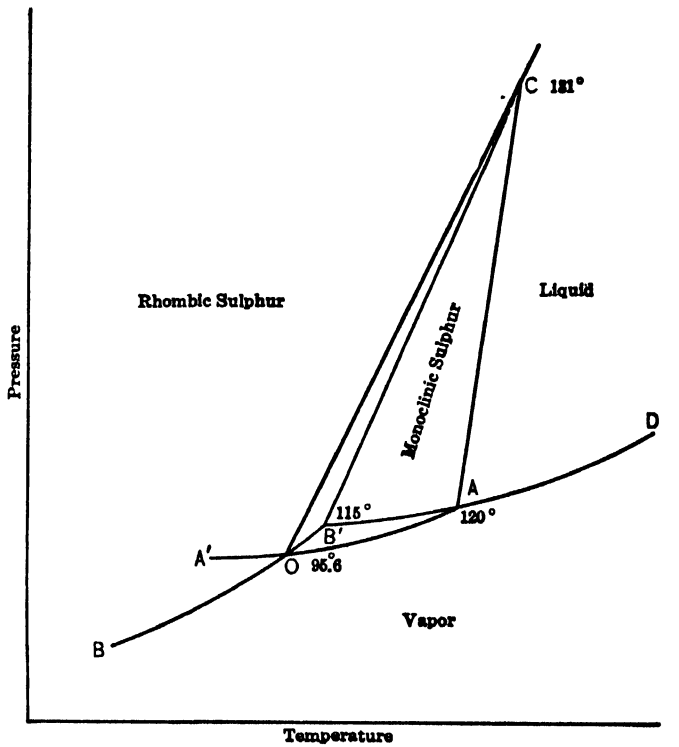

Fig. 108

phur are in equilibrium with sulphur vapor, this being a triple point, analogous to the point *O*, in Fig. 108. The vapor pressure curves of rhombic and monoclinic sulphur are represented by *OB* and *OA*, respectively. The dotted curve *OA'*, which is a continuation of *OA*, is the vapor-pressure curve of monoclinic sulphur in a metastable region. In like manner, *OB'* represents the vapor-pressure curve of rhombic sulphur in the metastable condition, *B'* being a metastable melting-point. As in the pressure-temperature diagram for water, the metastable phases have the higher

vapor pressure. The effect of increasing pressure on the transition point O, is represented by the line OC. This is termed a *transition curve.* Since increase in pressure raises the transition point, the line OC, slopes away from the vertical axis. The effect of increase of pressure on the melting-point of monoclinic sulphur, is shown by the curve AC. This also slopes away from the vertical axis, but the change in the melting-point of monoclinic sulphur produced by a given change in pressure being less than the corresponding change in the transition point, the two curves, OC and AC, intersect at the point C. The point C corresponds to a temperature of 131° C., and a pressure of 400 atmospheres. The vapor-pressure curve of stable liquid sulphur is represented by the curve AD. The vapor-pressure curve of the metastable liquid phase is represented by the curve AB', which is continuous with AD. The diagram is completed by the curve $B'C$, which represents the effect of pressure on the metastable melting-point of rhombic sulphur. Monoclinic sulphur does not exist above the point C. Hence, when liquid sulphur is allowed to solidify at pressures exceeding 400 atmospheres, the rhombic modification is formed, whereas under ordinary pressures the monoclinic modification appears first.

The phase rule enables us to state the exact conditions required for equilibrium, and to check the results of experiment. Thus, according to the formula, $C - P + 2 = F$, since $C = 1$, the system will be non-variant when $P = 3$. Since there are four phases involved, theoretically any three of these may be co-existent and four triple points are possible. The theoretically-possible triple points are as follows:

(1) Rhombic sulphur, monoclinic sulphur, and vapor (O);
(2) Rhombic sulphur, monoclinic sulphur, and liquid (C);
(3) Rhombic sulphur, liquid, and vapor (B');
(4) Monoclinic sulphur, liquid and vapor (A).

In this particular system all of the four possible triple points can be realized experimentally. That this is the case, is due to the comparative slowness of the change from rhombic to monoclinic sulphur above the triple point. If this change were rapid, it is evident that all of the theoretically-possible non-variant systems could not be realized experimentally.

As in the case of water, the curves in the diagram represent

univariant systems and the areas, bivariant systems. The student is advised to tabulate the univariant and bivariant systems represented in the pressure-temperature diagram for sulphur.

Two-Component Systems. When we apply the phase rule to systems of two components, we obtain, $2 - P + 2 = F$, or, in other words, we find that the maximum number of degrees of freedom possible, is three. Therefore, in order to represent a two-component system completely, three rectangular coördinate axes, representing temperature, pressure, and concentration, will be required. Such a space model is shown in Fig. 109. In this

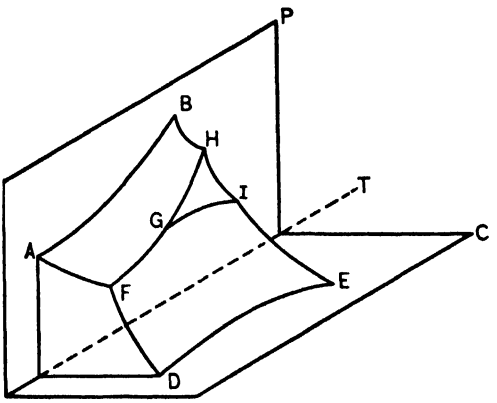

Fig. 109

three-dimensional diagram, any curve, such as AB lying in the P–T plane, represents change of pressure with temperature, the concentration remaining constant; any curve, such as AF lying in the P–C plane, represents change of pressure with concentration, the temperature remaining constant; in like manner, any curve, such as DE lying in the T–C plane, represents change in concentration with temperature, the pressure remaining constant. Any line on any one of the surfaces of the space model will represent the simultaneous variation of the three quantities — pressure, temperature, and concentration.

While three-dimensional models constructed in this manner undoubtedly give the most complete representation of two-component systems, it has been found that the various phase

relations can be depicted clearly and satisfactorily by passing planes through such space models, perpendicular to the three coordinate axes. It follows, therefore, that there will be three different sets of such diagrams corresponding to each model; namely, the *P–T* diagrams, the *T–C* diagrams and the *P–C* diagrams. Of these diagrams, the *P–T* and *T–C* diagrams are generally the most important. Among the different types of two-component systems which have been studied, may be mentioned systems involving anhydrous salts and water, hydrated salts and water, volatile solutes, two liquid phases, consolute liquids, and solid solutions.

We shall confine ourselves to the consideration of two-component systems, consisting of non-volatile solid solutes and liquid solvents. These systems may be conveniently classified as follows:

Class I. The two components crystallize together as a mixture of the pure components.

Class II. The two components crystallize together forming definite chemical compounds.

Class III. The two components crystallize together forming mixed crystals.

Class I. — $KCl + H_2O$. The *P–T* diagram of this system is shown in Fig. 110, together with the similar diagram for water alone, the latter being represented by dotted lines. At the triple point, *O*, ice and water have the same vapor pressure. Similarly, a solution at its freezing-point has the same vapor pressure as the ice which separates. The intersection of the vapor-pressure curve of ice, *OB*, and the vapor-pressure curve of the solution of the anhydrous salt, *O''A''*, determines a new triple point *O''*. Since the presence of the dissolved salt tends to diminish the vapor pressure of water, the curve *O''A''* is situated below the curve *OA*, and for the same reason, the triple point *O''* is found to the left of *O*. If an excess of dissolved substance is present, all of the liquid phases which are formed will of necessity be saturated solutions. When these solutions finally freeze, they will furnish, not pure ice, but a mixture of ice and solid salt, known as a *cryohydrate*. By a partial freezing, we can obtain the system: Solid salt, ice, saturated solution and vapor, or in other words, a system of $n + 2$ phases, which can exist only at the freezing temperature of the saturated solution, *T'*, and at the pres-

sure p', corresponding to the vapor pressure of ice and that of the saturated solution. These conditions are represented by the quadruple point O'. If we pass from the point O', increasing the temperature and pressure as prescribed by the curve $O'A'$, the ice will disappear, while the salt, the saturated solution, and the vapor will furnish a series of three-phase systems. Again start-

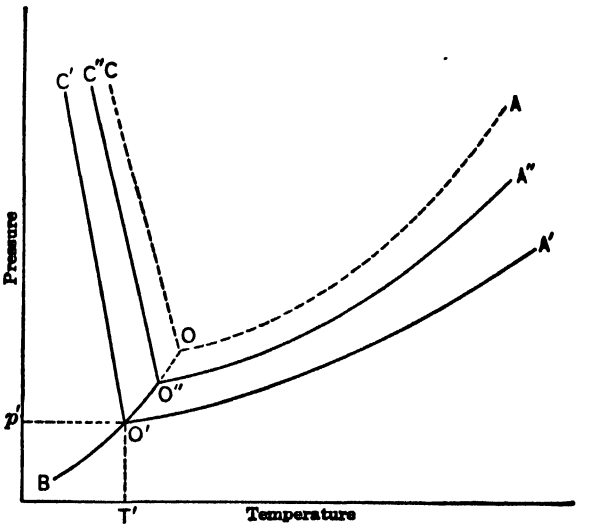

Fig. 110

ing from the point O', and lowering the temperature and the pressure, as indicated by the curve $O'B$, the liquid phase will disappear, while the solid salt, ice, and vapor will constitute another series of three-phase systems. This, of course, is on the supposition that the vapor pressure of the solid salt is negligible. Finally, a considerable increase in pressure will cause a slight lowering of the temperature of the quadruple point, O', as shown by the curve $O'C'$.

All possible non-saturated solutions of the salt will be represented by points within the area, $AOO'A'$. Thus, let $O''A''$ represent the vapor-pressure curve of a dilute aqueous solution of the salt. The freezing-point of this solution is represented by the point O'', while $O''C''$ represents the variation of the freezing-point of the solution with pressure. The following table summarizes the possibilities indicated by the phase rule:

(a) Areas. $(N - P + 2 = F)$, $2 - 2 + 2 = 2$, i.e., divariant systems:

Salt-vapor, below $A'O'B$ and above T-axis,
Solution-vapor, between $AOA'O'$,
Solution-ice, between $COO'C'$,
Ice-salt, between $C'O'B$ and P-axis.

(b) Curves. $(N - P + 2 = F)$, $2 - 3 + 2 = 1$, i.e., monovariant systems:

Solution-vapor-salt, $A'O'$,
Solution-ice-salt, $C'O'$,
Ice-salt-vapor, BO',
Solution-ice-vapor, OO'.

(c) Points. $(N - P + 2 = F)$, $2 - 4 + 2 = 0$, i.e., nonvariant system, O'.

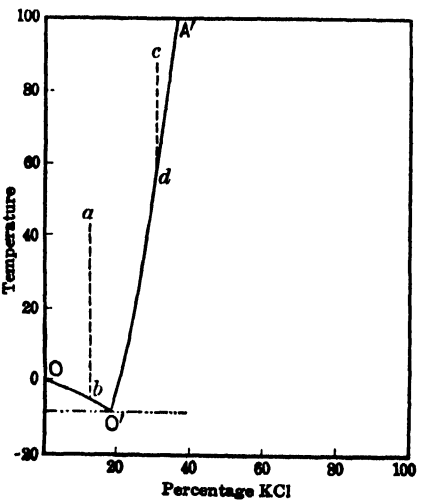

Fig. 111

The P–T diagram (Fig. 110) having been discussed, we now turn to the T–C diagram for the same system, Fig. 111. In this diagram, the abscissæ represent concentrations, and the ordinates, temperatures. For convenience, corresponding points in Figs. 110 and 111 will be designated by the same letters. The equilibrium between ice, water and water vapor, is represented by the point O. As the proportion of salt is increased, the tempera-

ture of equilibrium is lowered along the curve OO'. Ultimately, a point will be reached at which the solution becomes saturated, and on further addition of salt it will no longer dissolve but will remain in contact with the ice and saturated solution. This is the cryohydric point, and represents the lowest temperature which can be obtained in this particular system. The diagram is completed by the solubility curve of the salt, $O'A'$. Each point on this curve represents the concentration of a saturated solution down to the cryohydric temperature.

The meaning of the concentration-temperature diagram may be made clearer by a consideration of the behavior of a solution when gradually cooled. Let a represent a dilute solution of the anhydrous salt. On lowering the temperature along ab, no change will occur until the curve OO' is reached; then, ice will begin to separate, and as the cooling is continued, the composition of the solution will change along OO' until it reaches the cryohydric point O'. Here, both salt and ice will separate, and the solution will solidify completely at the temperature corresponding to the point O'. In like manner, if we start with a concentrated solution, represented by the point c, and cool along cd, no change will take place until the curve $O'A'$ is reached; then solid salt will separate and the composition of the solution will alter along $O'A'$, until the temperature is reduced to that corresponding to the cryohydric point, when the whole solution will solidify as in the previous case.

This phenomenon was first systematically investigated by Guthrie,* who concluded that such mixtures having constant composition and definite melting-point, are chemical compounds. Therefore, he proposed to call them cryohydrates. It has since been shown, that cryohydrates are not definite chemical compounds. Among the various reasons which have been advanced to prove the incorrectness of Guthrie's views, the following are the most convincing:— (1) the physical properties of a cryohydrate are the mean of the corresponding properties of the constituents, this being rarely true of chemical compounds; (2) the lack of homogeneity of a cryohydrate can be detected under the microscope; and (3) the constituents are seldom present in simple molecular proportions.

Class II. — $FeCl_3 + H_2O$. An interesting example of this class of two-component systems is furnished by mixtures of ferric

* Phil. Mag. [4], 49, 1 (1875); [5], 1, 49 and 2, 211 (1876).

chloride and water. This system has been very carefully investigated by Roozeboom.* The concentration-temperature diagram, plotted from Roozeboom's data, is given in Fig. 112. The freezing-point of pure water is represented by A, and the lowering of the freezing-point produced by the addition of ferric chloride is indicated by the curve AB. At the cryohydric temperature, $-55°$ C., ice, $Fe_2Cl_6 \cdot 12\ H_2O$, saturated solution, and vapor are in equilibrium, and the system is non-variant. On adding more

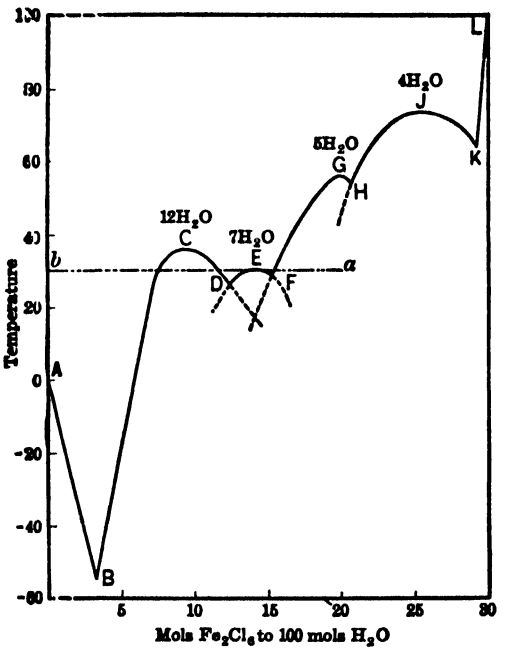

Fig. 112

ferric chloride, the ice phase disappears, and the univariant system, $Fe_2Cl_6 \cdot 12\ H_2O$, saturated solution, and vapor results. The equilibrium is represented by the curve BC, which may be regarded as the solubility curve of the dodecahydrate. On continuing the addition of ferric chloride, the temperature of equilibrium rises until the point C is reached. Here the composition of the solution is identical with that of the dodecahydrate, and, therefore, the temperature corresponding to this point, 37° C., may be looked upon as the melting-point of $Fe_2Cl_6 \cdot 12\ H_2O$. Further

* Zeit. phys. Chem., 4, 31 (1889); 10, 477 (1892).

addition of ferric chloride, will naturally lower the melting-point, and the equilibrium will alter along the curve *CD*. It is thus possible to have two saturated solutions (at the same temperature) one of which contains more water, and the other less, than the hydrate which is in equilibrium with the solution. These solutions are both stable throughout, and are nowhere supersaturated. Roozeboom was the first investigator to discover a saturated solution containing less water than the solid hydrate with which it is in equilibrium. This discovery led him to define supersaturation as follows: — "A solution is supersaturated with respect to a solid phase, at a given temperature, if its composition is between that of the solid phase and the saturated solution." At the point *D*, the curve reaches another minimum, which is analogous to the point *B*, except that the heptahydrate, $Fe_2Cl_6 \cdot 7\,H_2O$, takes the place of ice. Here we have equilibrium between, the dodecahydrate, the heptahydrate, saturated solution, and vapor, and the system is non-variant. On further addition of ferric chloride, another maximum is reached at *E*, corresponding to the melting-point of the heptahydrate. In a similar manner, two other maxima at greater concentrations of ferric chloride, reveal the existence of the hydrates, $Fe_2Cl_6 \cdot 5\,H_2O$, and $Fe_2Cl_6 \cdot 4\,H_2O$. At the three remaining quadruple points the following phases are in equilibrium: At F, $Fe_2Cl_6 \cdot 7\,H_2O$, $Fe_2Cl_6 \cdot 5\,H_2O$, saturated solution and vapor; at H, $Fe_2Cl_6 \cdot 5\,H_2O$, $Fe_2Cl_6 \cdot 4\,H_2O$, saturated solution and vapor; and at K, $Fe_2Cl_6 \cdot 4\,H_2O$, Fe_2Cl_6, saturated solution and vapor. The solubility of the anhydrous salt is represented by the curve, *KL*. Metastable solubility and melting-point curves are represented by dotted lines.

The student should apply the phase rule to this system. If a fairly dilute solution of ferric chloride is evaporated at 31° C., the water gradually disappears, and a residue of the dodecahydrate remains. This residue then liquefies, and again dries down, the composition of the residue corresponding to the heptahydrate: on further standing, the phenomenon is repeated, the final and permanent residue having a composition corresponding to the pentahydrate. The dotted line, *ab*, shows the isothermal along which the composition varies. It would have been a difficult matter to explain the alternations of moisture and dryness, observed in this experiment, without the concentration-temperature diagram.

Class III. In all of the two-component systems thus far considered, the composition of the solid phase has remained constant, while that of the liquid phase has undergone continuous variation. In the systems belonging to Class III, however, the solid phase which separates from the solution, on cooling, is found to contain both components in continuously varying proportions. It follows, therefore, that two-component systems belonging to this class consist of *two* solutions, one a *liquid solution* and the other a *solid solution*, in equilibrium with each other. Obviously, the complete temperature-concentration diagram must contain two curves, one of which corresponds to the liquid, and the other to the solid, solution. The upper curve, corresponding to the liquid solution, is commonly called the *liquidus curve*, while the lower curve, corresponding to the solid solution, is known as the *solidus curve*. The substitution of the terms, *crystallization-point curve*, and *melting-point curve*, for the terms liquidus and solidus curves, is greatly to be preferred. The region above the curves, represents liquid solutions, while the region below the curves, represents solid solutions. There are three distinct types of melting-point curves for solid solutions in which the two components are miscible in all proportions: namely, Type I, in which the freezing-points of all mixtures lie between those of the two components; Type II, in which a certain mixture has a maximum freezing-point; and Type III, in which a particular mixture has a minimum freezing-point.

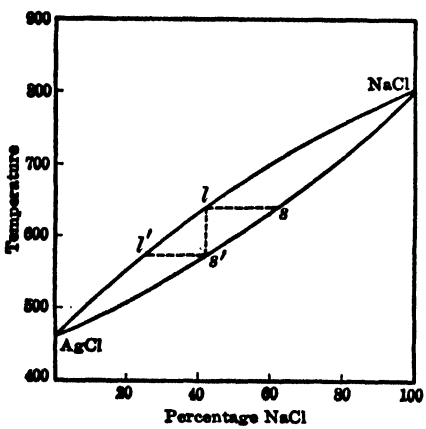

Fig. 113

The general characteristics of a two-component system belonging to Type I, may be illustrated by the temperature - concentration diagram of the system AgCl – NaCl, as shown in Fig. 113. If the temperature of a fused mixture of these two salts, having the composition represented by the point *l* on the crystallization point curve, be gradually lowered, a solid phase, having the composition

represented by s, will separate out. If the temperature be lowered very slowly, so as to insure the homogeneity of the solid phase, the composition of the final portion of the solution to solidify, will correspond to that of the point s', and the composition of the remaining liquid solution will be represented by the point l'. The temperature interval represented by the line, ls', is known as the *crystallization interval.* If care is not taken to cool the solution gradually, the solid phase will not become homogeneous, owing to the slow rate of diffusion of the two components in the mixture, and consequently the final temperature of solidification will be considerably lower than that corresponding to the point s'. This precaution is of great practical importance in connection with the preparation of alloys, where the rate of diffusion of the constituents is necessarily slow.

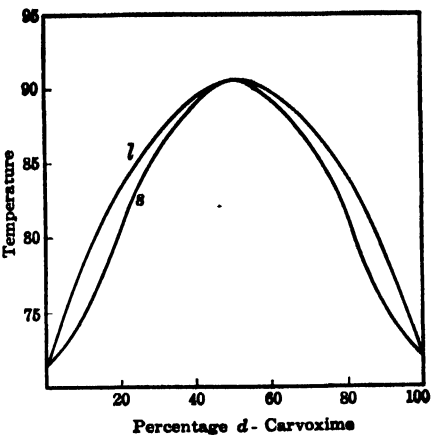

Fig. 114

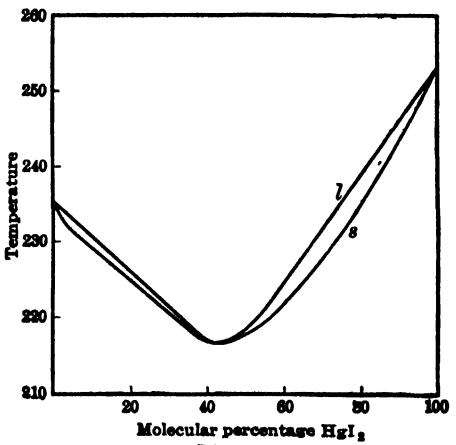

Fig. 115

Illustrations of the two remaining types of binary mixtures which form mixed crystals are shown in the accompanying diagrams. The diagram of the system, *d*- and *l*-carvoxime ($C_{10}H_{14}N.OH$), shown in Fig. 114,* furnishes an example of Type II, while Type III is illustrated by the system $HgBr_2 - HgI_2$,† a diagram of

* Adriani, Zeit. phys. Chem., 33, 469 (1900).

† Reinders, ibid., 32, 494 (1900).

which is shown in Fig. 115. It will be seen, that the curves shown in Figs. 113, 114 and 115, are exactly analogous to the three types of boiling-point curves of binary mixtures which have been discussed in an earlier chapter (see p. 198).

A large number of binary systems are known in which the two components do not form a continuous series of mixed crystals. This case, which is perfectly analogous to that of the partial miscibility of liquids, may be illustrated by the system, $KNO_3 - TlNO_3$, a diagram of which is shown in Fig. 116. At the temperature corresponding to C, two solid solutions having compositions corresponding to, D and E, separate out, the temperature remaining constant until all of the liquid has solidified. On lowering the temperature below C, the two solid solutions, which were in equilibrium at C, undergo a change in composition, as indicated by the dotted lines.

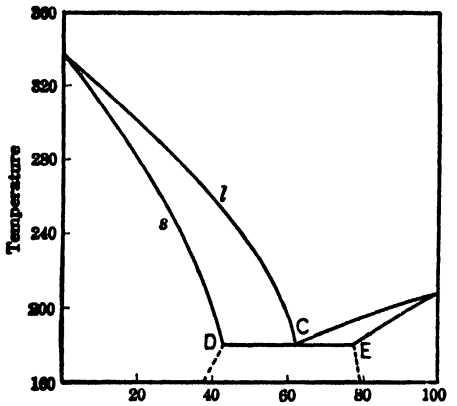

Fig. 116

Three-Component Systems. According to the phase rule, the number of degrees of freedom in a three-component system will be given by the expression, $3 - P + 2 = F$. It is evident, therefore, that the system will become invariant when five phases, — the maximum number possible in a three-component system — are co-existent. Since, at least one phase must be present, the maximum number of degrees of freedom will be four, the variables being temperature, pressure, and the ratios of two of the components to the remaining component in any single phase.

In the graphic representation of three-component systems, use is commonly made of the triangular diagram. This consists of an equilateral triangle, each side of which is divided into one hundred equal parts, corresponding to 100 per cent of each of the three pure components, which are represented by the apices of the triangle. For example, if it is desired to represent on a triangular diagram, a ternary mixture consisting of x per cent of A, y per

cent of B and z per cent of C, we would first measure off on AB, in the triangular diagram shown in Fig. 117, x units from B and y units from A, and then through the points so obtained, draw lines parallel to BC and AC respectively. The point, P, at which these two lines intersect, will represent the ternary mixture having the composition given above. Should it be desired to represent, simultaneously, the variation of the equilibrium with temperature, this can readily be accomplished by plotting the latter on an axis perpendicular to the plane of the triangular diagram.

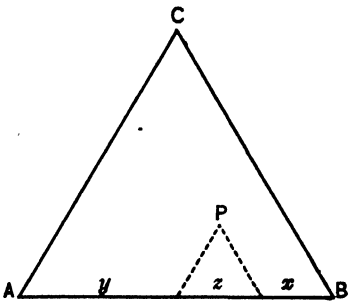

Fig. 117

Owing to the complexity of three-component systems, we shall limit our treatment of these systems to a brief consideration of one or two relatively simple cases.

The system, chloroform-water-acetic acid, which has been thoroughly investigated by Wright,* furnishes an interesting example of a ternary liquid mixture, in which the three components form a single pair of partially miscible liquids. At ordinary temperatures, water and chloroform are only slightly soluble in each other, while each of these liquids is miscible with acetic acid in all proportions. The equilibrium relations in this system, at 18° and under constant pressure, are shown graphically in Fig. 118. Since both temperature and pressure are assumed to be constant, there are three degrees of freedom. If we have but a single homogeneous phase, it will have two degrees of freedom, and in

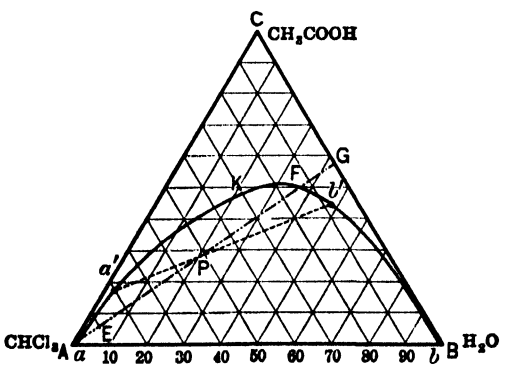

Fig. 118

* Proc. Roy. Soc., 49, 174 (1891); 50, 375 (1892).

consequence, will be represented by some point within a definite region. In like manner, if we have two liquid phases, the system will be univariant, and therefore, will be represented by some point on the curve aKb. On adding water to chloroform, we obtain a homogeneous solution, provided the amount of water does not exceed that corresponding to complete saturation, represented by the point a. If further amounts of water are added, the mixture will separate into two layers, one of which consists of a saturated solution of water in chloroform, and the other, a saturated solution of chloroform in water. The composition of these two conjugate solutions is represented by the points, a and b. If now, acetic acid is added, it will distribute itself between the two layers, forming two conjugate ternary solutions of chloroform, water and acetic acid which are in equilibrium with each other. These solutions are represented by two points, such as a' and b', within the triangular diagram. The line joining a' and b' is known as a *tie-line;* as is generally the case, this line is not parallel to the base of the triangle ABC. As more and more acid is added, the tie-lines become shorter and shorter, and ultimately, when the compositions of the two conjugate solutions become identical, they shrink to the single point, K. The point K is, therefore, a *critical point,* since further addition of acetic acid will result in the formation of a single homogeneous phase. Any point within the curve, represents a ternary mixture which will separate into two conjugate liquid phases, while any point without the curve, represents a single homogeneous liquid phase. Since we have a bivariant system made up of three components, existing in two liquid phases and one vapor phase, it follows, that the composition of the two conjugate solutions, and the total vapor pressure, will depend, not only on the temperature, as in the case of two-component systems, but also on the initial composition of the mixture. If the total vapor pressure be assumed to remain constant, the composition of the different conjugate ternary solutions will vary with the temperature alone. At the point K, where the two liquid phases become identical, the number of degrees of freedom is reduced to one, and therefore, the critical point is seen to be dependent upon the temperature alone. As has been pointed out, a ternary mixture whose composition is represented by the point P, will separate into two conjugate ternary solutions having the compositions, a' and b'. If a line be

drawn from A through P, cutting the isotherm aKb in E and F, and the line BC in G, it can be shown, that in all mixtures represented by points on AG, the ratio of the components, B and C, is constant, and equal to GB/GC. If to a mixture of water and acetic acid whose composition is represented by the point G, increasing amounts of chloroform be added, we shall obtain in succession, (1) a series of homogeneous solutions between G and F, (2) a series of heterogeneous mixtures of two conjugate solutions between F and E, and (3) another series of homogeneous solutions between E and A.

Owing to the fact that acetic acid does not distribute itself equally between water and chloroform, the critical point K lies below the highest point of the curve Hence, by selecting a homogeneous solution in which the concentration of the acetic acid is greater than that corresponding to the critical point K, but less than that represented by the summit of the curve, it is possible, by adding the proper amounts of the three components, to maintain the concentration of the acetic acid constant, and yet pass along a horizontal line from a homogeneous region, through a heterogeneous region, into a homogeneous region again. This phenomenon is known as *retrograde solubility*, and is encountered in all cases where the critical point lies below the highest point of the isothermal curve.

We will now consider very briefly, two other typical three-component systems, involving two, and three pairs of partially miscible liquids, respectively.

The system water-aniline-phenol, which has been investigated by Schreinemakers,* may be taken as an example of a three-component system containing two pairs of partially miscible liquids, namely water and aniline, and water and phenol. This system is represented, diagrammatically, in Fig. 119, three different isothermals being given. The interpretation of this diagram should be fully written out by the student.

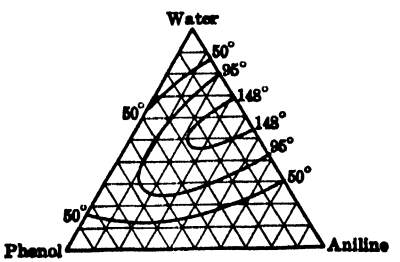

Fig. 119

The system, water-ether-succinic nitrile, also investigated by

* Zeit. phys. Chem., 29, 577 (1898).

Schreinemakers,* furnishes an example of a three-component system containing three pairs of partially miscible liquids. This system is represented in the diagram, shown in Fig. 120. The compositions of all mixtures forming single homogeneous solutions are represented by points in the unshaded areas of the triangular diagram. All points lying within the shaded quadrilateral areas, represent mixtures which form two liquid layers, while all points included within the shaded triangular area, represent mixtures which break up into three liquid layers of the composition *a*, *b* and *c*.

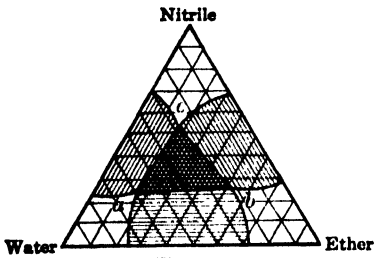

Fig. 120

Alloys. The phase rule has proven to be of inestimable value in the investigation of intermetallic mixtures, commonly known as *alloys*. In the study of these substances, the determination of the freezing-point curve is of fundamental importance, since, from its characteristics, an insight into the nature of the solid and liquid phases involved can generally be obtained. It has already been pointed out, that the freezing-point curves of two-component systems may conveniently be divided into the three following types: — Type I, in which the pure components separate out from the mixture; Type II, in which the components form one or more compounds with each other; and Type III, in which the components form mixed crystals. Representatives of each of these types are found among the alloys.

Owing to the fact, that the temperatures at which most alloys melt are relatively high, and also because of the difficulty of bringing about the separation of the different solid phases free from contamination with the other phases, it is customary to employ the method of *thermal analysis* in the investigation of the freezing-points of alloys. This method is based upon the experimental determination of the cooling curves of molten mixtures of the given metals in varying proportions. The curve obtained by plotting temperature against time, when a two-component liquid system is allowed to cool slowly by radiation, is called the *cooling curve*. This curve is logarithmic when the temperature

* Zeit. phys. Chem., 23, 543 (1898).

of the environment is constant, but becomes rectilinear, if the surrounding temperature is regularly and progressively lowered. So long as the system consists of a single liquid phase, the cooling curve will remain smooth and continuous, as shown by AB in Fig. 121a, but should a second phase appear, a sudden discontinuity in the curve will occur simultaneously, as shown by BC in the diagram. If the new phase has the same composition as the liquid phase, the temperature will remain constant, as in the diagram, until all of the liquid phase has disappeared. On the other hand, if the new phase differs in composition from that of the liquid phase, the cooling curve will undergo a somewhat abrupt change in direction, due to the fact, that the composition of the liquid phase alters continuously as the temperature falls. If a third phase is formed, the temperature of the system will remain constant, until one of the phases has completely disappeared. The cooling curve of a two-component liquid system, in which the first phase to separate has a different composition from that of the liquid phase, is shown in Fig. 121b. Here EF represents the cooling curve of the liquid; F, the appearance of the second phase differing in composition from that of the liquid phase, while H represents the appearance of a third phase. During the separation of the latter, the temperature of the system remains constant, after which it cools uniformly along IK.

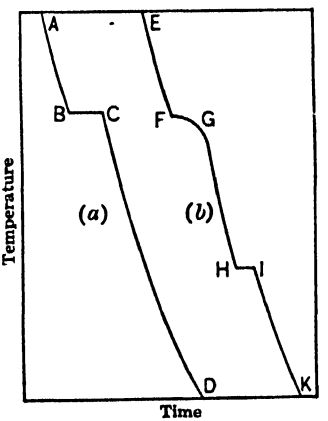

Fig. 121

The System, Zinc-Cadmium. A brief consideration of the two-component system, zinc-cadmium, will serve to illustrate the application of the method of thermal analysis to the study of alloys. In this system, the two components are not miscible in the solid state and do not form intermetallic compounds. In order to determine the curves of equilibrium, mixtures of the two metals, in varying proportions, are fused, and then allowed to cool slowly, the rate of cooling being measured by means of a thermocouple, one junction of which is maintained at constant tempera-

ture, while the other junction is placed in the mixture. The terminals of the thermocouple are connected to a sensitive galvanometer, graduated to read directly in degrees, and the rate of cooling is followed by the movement of the needle of the galvanometer. The cooling curves, thus obtained, for each of the two components, and for nine mixtures containing increasing amounts of cadmium, are plotted in the diagram, shown in Fig. 122. Let

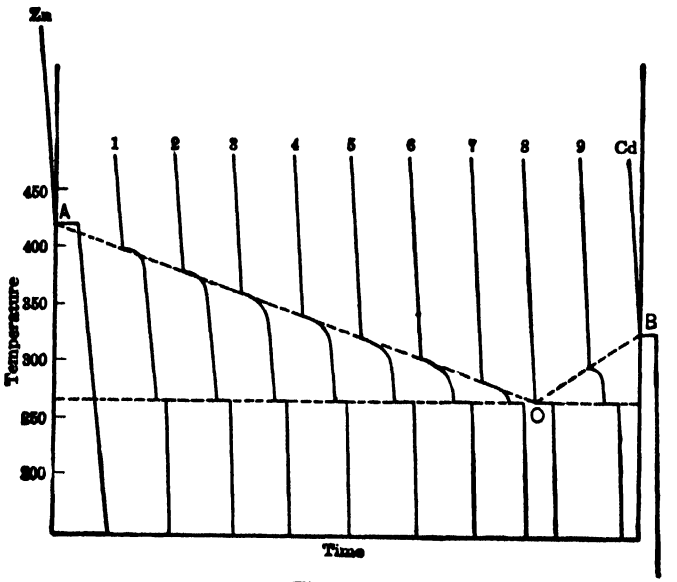

Fig. 122

us take, for example, cooling curve No. 2, corresponding to a liquid mixture which is relatively rich in zinc. As the temperature falls, a point will ultimately be reached at which pure zinc begins to crystallize, and since the temperature remains constant during the crystallization, a break occurs in the cooling curve. This first break is the freezing-point of the mixture, and determines a point on the curve *AO*. As zinc continues to separate, the composition of the mixture changes along *AO*, until *O* is reached: here the mixture is saturated with respect to cadmium, and both metals separate as a conglomerate, having the same composition as the fused mixture. The separation of the latter phase causes the second break in the cooling curve, the temperature remaining constant until the entire mass has solidified. It will be noticed,

that this system is the exact analogue of the system — anhydrous salt and water. The point *O*, which corresponds to the cryohydric point, is called the *eutectic point*, and the composition of the mixture having this minimum melting-point, is known as the *eutectic mixture*. From the cooling curve diagram we can construct the equilibrium diagram, shown in Fig. 123.

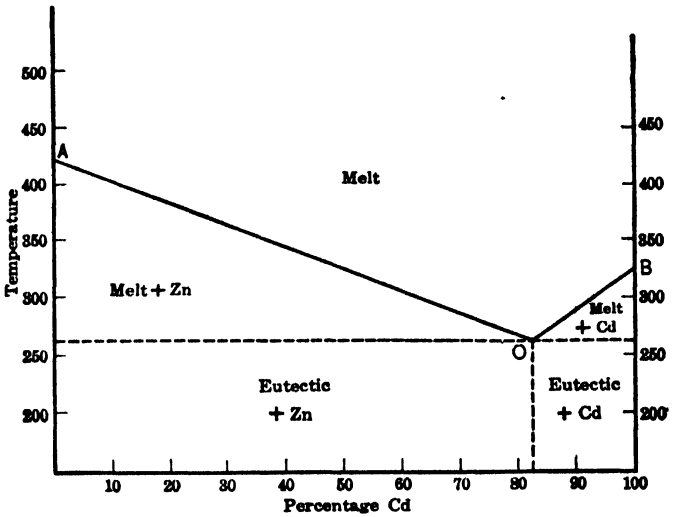

Fig. 123

The System, Gold-Aluminium. A binary system belonging to Type II, in which the components form several compounds with each other, is the system, gold-aluminium, which has been studied by Heycock and Neville.* The concentration-temperature diagram of this system, which is shown in Fig. 124, reveals the existence of definite compounds, Au_5Al_2, Au_2Al, and $AuAl_2$, corresponding to the points *D*, *E* and *H*, respectively. The discontinuities at *B* and *G* suggest the possibility of two other compounds, viz., Au_4Al and AuAl. The diagram shows that the following substances will crystallize in succession from the molten alloy, these being the different solids with which the liquid mixture is saturated in its successive stages of equilibrium:

Curve *AB*, pure gold at *A*;
Curve *BC*, Au_4Al, nearly pure at *B*;
Curve *CD*, Au_5Al_2 or Au_3Al_2, nearly pure at *D*;

* Phil. Trans. A., 194, 201 (1900).

Curve *DEF*, Au_2Al, pure at *E*;
Curve *FG*, AuAl, maximum undetermined,
Curve *GHI*, $AuAl_2$, pure at *H*;
Curve *IJ*, Al, pure at *J*.

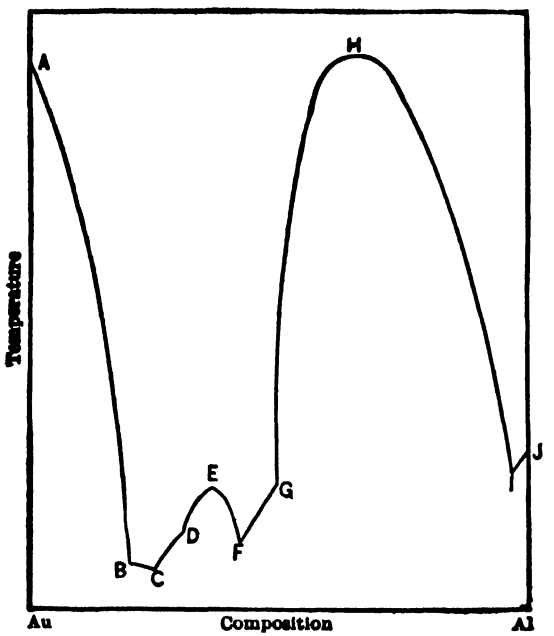

Fig. 124

The points *C*, *F*, and *I* represent non-variant systems, the melting-points of the respective eutectic alloys being 527°, 569°, and 647°. This system in many respects resembles the system — ferric chloride and water.

For a further discussion of the phase rule and its applications, the student must consult the references listed below.

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The Phase Rule and its Applications. Findlay.
The Phase Rule. Bancroft.
Physical Chemistry of the Metals. Schenck. Translated by Dean. Chapters II and III.
Metallic Alloys. Gulliver.
Metallography. Desch. Chapters II to V inclusive.
The Crystallisation of Iron and Steel. Mellor.
Treatise on Physical Chemistry. Taylor. Chapter IX.

PROBLEMS

1. The vapor pressure of solid NH_4HS at 25°.1 is 50.1 cm. Assuming that the vapor is practically completely dissociated into NH_3 and H_2S, calculate the total pressure at equilibrium when solid NH_4HS is allowed to dissociate at 25°.1 in a vessel containing ammonia at a pressure of 32 cm. *Ans.* 59.5 cm.

2. In the partition of acetic acid between CCl_4 and water, the concentration of the acetic acid in the CCl_4 layer was c gram-molecules per liter and in the corresponding water layer w gram-molecules per liter.

c	0.292	0.363	0.725	1.07	1.41
w	4.87	5.42	7.98	9.69	10.7

Acetic acid has its normal molecular weight in aqueous solutions. From these figures show that, at these concentrations, the acetic acid in the carbon tetrachloride solution exists as double molecules.

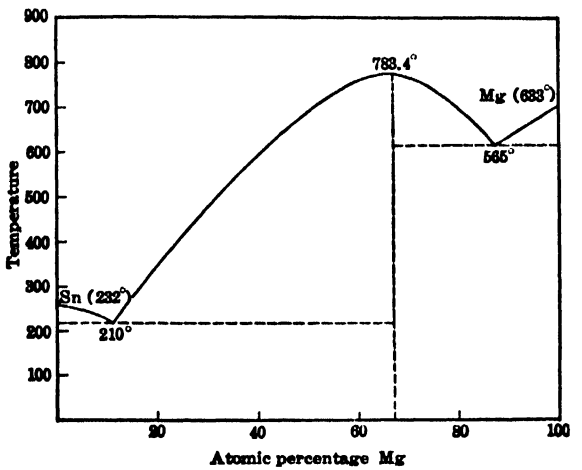


Fig. 125

3. Acetic acid distributes itself between water and benzene in such a manner that in a definite volume of water there are 0.245 and 0.314 gram of the acid, while in an equal volume of benzene there are 0.043 and 0.071 gram. What is the molecular weight of acetic acid in benzene, assuming it to be normal in water? *Ans.* 121.3.

4. The salt $Na_2HPO_4.12\,H_2O$ has a vapor pressure at 15° of 8.84 mm., and at 17°.3 of 10.53 mm. Calculate the heat of vaporization, i.e., the thermal change during the loss of 1 mol of water at crystallization by evaporation. *Ans* 12,651 cal.

5. The solubility of boric acid in water is 38.45 grams per liter at 13°, and 49.09 grams per liter at 20°. Calculate the heat of solution of boric acid per mol. *Ans.* 5822 cal.

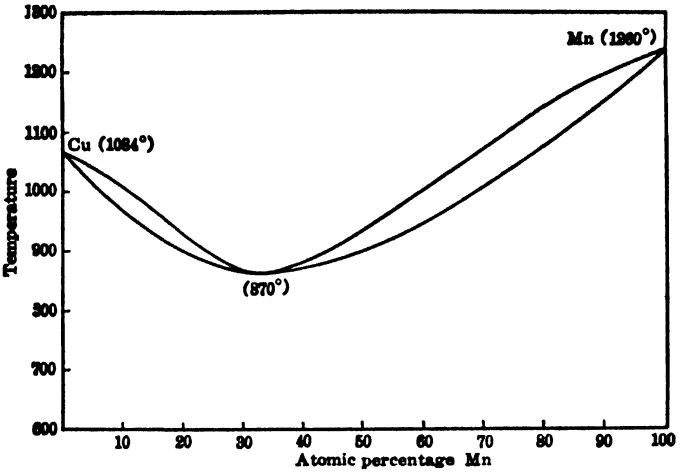


Fig. 126

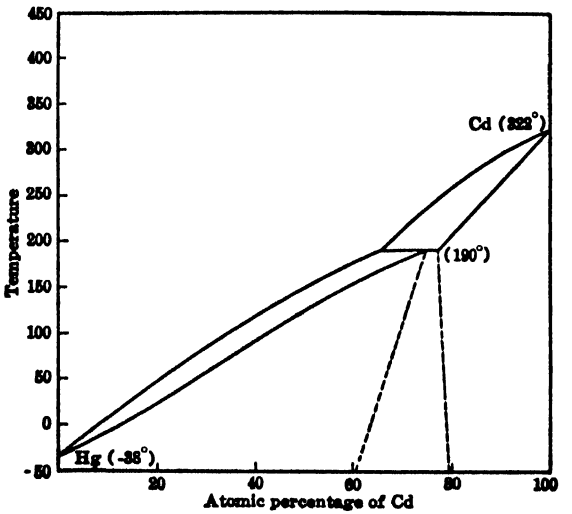


Fig. 127

6. Plot the pressure-temperature diagram for calcium carbonate from the table given on p. 385, and apply the phase rule.

7. Is it possible to decide by the phase rule whether the eutectic alloy is a mixture or a compound?

8. By means of the principle of Le Chatelier, verify as far as possible the statement made on p. 398 relative to the densities of the different forms of ice discovered by Tammann and Bridgman. Make use of the diagram shown in Fig. 107.

9. Which has the greater density, (a) monoclinic sulphur or rhombic sulphur; (b) rhombic sulphur or liquid sulphur; (c) monoclinic sulphur or liquid sulphur?

10. How do you explain the action of freezing mixtures, such as ice and common salt?

11. Why is it that cryohydrates can be used as constant temperature baths?

12. Interpret the temperature-composition diagram for the system, tin-magnesium, shown in Fig. 125.

13. Interpret the temperature-composition diagram for the system, copper-manganese, shown in Fig. 126.

14. Interpret the temperature-composition diagram for the system, mercury-cadmium, shown in Fig. 127.

CHAPTER XIV

CHEMICAL KINETICS

Velocity of Reaction. In the two preceding chapters we have considered the equilibrium which is established when the speeds of the direct and reverse reactions have become equal. We now proceed to consider the velocity of individual reactions. By far the greater number of the reactions between inorganic substances, proceed with such rapidity that it is impossible to measure their velocities. Thus, when an acid is neutralized by a base, the indicator changes color almost instantly. There are a few well-known reactions which are exceptions to this rule; among these may be mentioned the oxidation of sulphur dioxide, and the decomposition of hydrogen peroxide. Both of these reactions are well adapted to kinetic experiments. In organic chemistry, on the other hand, slow reactions are the rule rather than the exception. Thus the reaction between an alcohol and an acid, forming an ester and water, proceeds very slowly under ordinary conditions, and the progress of the reaction may be easily followed. By means of the law of mass action, it is possible to derive equations expressing the velocity of a reaction at any moment, in terms of the concentrations of the reacting substances present at that time.

Let the equation,

$$A_1 + A_2 \rightleftarrows A_1' + A_2',$$

represent a reversible reaction and let a, b, c, and d be the respective initial concentrations of the reacting substances A_1, A_2, A_1', and A_2'. The velocity of the direct reaction will then be

$$\frac{dx}{dt} = k\,(a - x)\,(b - x), \tag{1}$$

where k is the velocity constant, and dx is the infinitely small increase in the amount of x, during the infinitely small interval of time dt. Similarly, the velocity of the reverse reaction will be

$$\frac{dx'}{dt} = k_1\,(c + x)\,(d + x). \tag{2}$$

It is evident, that the substances on the right-hand side of the equation will exert an ever-increasing influence upon the velocity of the direct reaction, which must accordingly decrease. When, however, the velocities of the direct and reverse reactions become equal, equilibrium will be established, and the ratio of the amounts of the reacting substances on the two sides of the equation will remain constant. The total velocity due to these opposing reactions will be

$$\frac{dX}{dt} = \frac{dx}{dt} - \frac{dx'}{dt} = k\,(a - x)\,(b - x) - k_1\,(c + x)\,(d + x), \quad (3)$$

and at equilibrium, when $\frac{dX}{dt} = 0$,

$$k\,(a - x)\,(b - x) = k_1\,(c + x)\,(d + x),$$

or

$$\frac{(c + x)\,(d + x)}{(a - x)\,(b - x)} = \frac{k}{k_1} = K_c. \quad (4)$$

This equation has been thoroughly tested in the two preceding chapters. Thus, in the reaction,

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

K_c has been shown to have the value, 2.84, at ordinary temperatures. The velocity constants of the direct and reverse reactions have also been determined, the values being, $k = 0.000238$ and $k_1 = 0.0000815$. When these values are substituted in the equation, $\frac{k}{k_1} = K_c$, we obtain $K_c = 2.92$, a value which agrees well with that found by direct experiment. The application of equation (3) is much simplified by the fact that most reactions proceed nearly to completion in one direction, so that the term, $k_1\,(c + x)\,(d + x)$, will be so small that it may be neglected. We then have,

$$\frac{dx}{dt} = k\,(a - x)\,(b - x), \quad (5)$$

an equation expressing the velocity of the direct reaction in terms of the concentrations of the reacting substances.

Unimolecular Reactions. The simplest type of chemical reaction is that in which the concentration of only one substance undergoes change, and in which the velocity of the reverse reaction

is negligible. The decomposition of hydrogen peroxide is an example of such a reaction. In the presence of a catalyst, such as certain unorganized ferments, or colloidal platinum, hydrogen peroxide decomposes as represented by the equation,

$$H_2O_2 \rightleftarrows H_2O + \tfrac{1}{2} O_2.$$

This reaction is usually allowed to take place in dilute aqueous solution, so that there is no appreciable alteration in the amount of solvent throughout the entire course of the reaction. Furthermore, the activity of the catalyst remains constant, so that the course of the reaction is wholly determined by the concentration of the hydrogen peroxide. A very satisfactory catalyst is catalase, an enzyme derived from blood. The concentration of hydrogen peroxide present at any time during the reaction, can be determined very simply by removing a definite portion of the reaction mixture, adding an excess of sulphuric acid to destroy the activity of the catalase, and then titrating with a standard solution of potassium permanganate.

The following table gives the results of such an experiment: —

DECOMPOSITION OF H_2O_2 BY CATALASE

t (minutes).	$a - x$, cc. $KMnO_4$.	x, cc. $KMnO_4$.	k
0	46.1	0	.....
5	37.1	9.0	0.0435
10	29.8	16.3	0.0438
20	19.6	26.5	0.0429
30	12.3	33.8	0.0440
50	5.0	41.1	0.0444
			Mean 0.0437

The second column of the table gives the number of cubic centimeters of the potassium permanganate solution required to oxidize 25 cc. of the reaction mixture, when the time intervals recorded in the first column have elapsed after the introduction of the catalyst. Since the numbers in the second column, represent the actual concentration of hydrogen peroxide present at the end of the successive intervals of time, it is evident, that the difference between these numbers and 46.1 cc. — the initial concentration of hydrogen peroxide — will give the amounts of peroxide decomposed in those intervals. These numbers are

recorded in the third column of the table. It will be seen, that as the concentration of the hydrogen peroxide decreases, the rate of the reaction diminishes. Thus, in the first interval of 10 minutes, an amount of hydrogen peroxide corresponding to 46.1 − 29.8 = 16.3 cc. of potassium permanganate is decomposed, while in the second interval of 10 minutes, the amount of hydrogen peroxide decomposed is equivalent to 29.8 − 19.6 = 10.2 cc. of potassium permanganate. Since only a single substance is undergoing change, equation (5) simplifies to the following form:

$$\frac{dx}{dt} = k\,(a - x).$$

It is impossible to apply the equation in this form, since in order to obtain accurate titrations, dt must be taken fairly large, and during this interval of time, $a - x$ will have diminished. Approximate values of k may be obtained, by taking the average value of $a - x$, during the interval dt, within which an amount dx of hydrogen peroxide is being decomposed. For example, let us take the interval between 5 and 10 minutes; dx = 16.3 − 9.0 = 7.3 cc., dt = 5 min., and the average value of $a - x$ is

$$\frac{37.1 + 29.8}{2} = 33.45 \text{ cc.}$$

Substituting in the equation,

$$\frac{dx}{dt} = k\,(a - x),$$

we have

$$\frac{7.3}{5} = k \times 33.45,$$

and

$$k = 0.0436.$$

Similarly, taking the next interval between 10 and 20 minutes; dx = 26.5 − 16.3 = 10.2 cc., dt = 10 minutes, and the average value of $a - x$ is, $\frac{29.8 + 19.6}{2}$ = 24.7 cc. Substituting in the equation as before, we obtain

$$\frac{10.2}{10} = k \times 24.7,$$

and

$$k = 0.0413.$$

As will be seen, these two values of k are not in good agreement, although the first value of k agrees closely with the mean value of k, given in the fourth column of the table.

In order to apply the equation,

$$\frac{dx}{dt} = k\,(a - x)\,,$$

it must be integrated.

The integration of this equation may be performed as follows: —

$$\frac{dx}{dt} = k\,(a - x),$$

therefore,

$$\frac{dx}{a - x} = k\,dt.$$

Integrating, we have

$$\int \frac{dx}{a - x} - \int k\,dt = \text{constant} = C,$$

therefore,

$$-\log_e (a - x) - kt = C.$$

In order to determine C, the constant of integration, we make use of the experimental fact, that when $t = 0$, $x = 0$. Substituting these values, we have

$$-\log_e a = C.$$

Consequently

$$\log_e a - \log_e (a - x) = kt,$$

or

$$\frac{1}{t}\log_e \frac{a}{a - x} = k. \qquad (6)$$

Passing to Briggsian logarithms, we obtain,

$$\frac{1}{t}\log \frac{a}{a - x} = 0.4343\,k. \qquad (7)$$

By substituting in this equation, the corresponding values of a, $a - x$, and t, from the preceding table, the values of k given in the fourth column of the table are obtained.

The equation,

$$\frac{dx}{dt} = k\,(a - x),$$

may also be thrown into an exponential form, as follows:

Since,

$$\frac{1}{t}\log_e \frac{a}{a - x} = k,$$

we may write,

$$-kt = \log_e \frac{a - x}{a},$$

or

$$a - x = ae^{-kt},$$

and

$$x = a\,(1 - e^{-kt}). \tag{8}$$

In this equation, k may be regarded as the fraction of the total amount of substance decomposing in the unit of time, provided this unit is so small, that the quantity at the end of the time is only slightly different from that at the beginning. The time required for one-half of the substance to change, is known as the period of half-change, T, and may be calculated from k by means of the equation,

$$\log 2 = 0.4343\,kT,$$

therefore,

$$T = 0.6943\frac{1}{k}, \tag{9}$$

or

$$\frac{1}{k} = 1.443\ T. \tag{10}$$

Reactions in which only one mol of a single substance undergoes change in concentration, are known as *unimolecular reactions*, or *reactions of the first order*. In a unimolecular reaction, the velocity constant, k, is independent of the units in which concentration is expressed. If, in the integrated equation,

$$kt = \log_e \frac{a}{a - x},$$

t becomes infinite, then $x = a$. In other words, for finite values of t, x must always remain less than a and the reaction will never proceed to completion.

Another unimolecular reaction which has been thoroughly

investigated, is the hydrolysis of cane sugar. When cane sugar is dissolved in water, containing a small amount of free acid, it is slowly transformed into d-glucose and d-fructose. The velocity of the reaction is very small, and is dependent upon the strength of the acid added. The progress of the reaction may be very easily followed by means of the polarimeter. Cane sugar is dextro-rotatory, while d-fructose rotates the plane of polarization more strongly to the left than d-glucose rotates it to the right. Therefore, as the hydrolysis proceeds, the angle of rotation to the right steadily diminishes until, when the reaction is complete, the plane of polarization will be found to be rotated to the left. On this account, the hydrolysis of cane sugar is commonly termed *inversion*, and the molecular mixture of d-fructose and d-glucose, constituting the product of the reaction, is called *invert sugar*. Let α_0 denote the initial angle of rotation, at the time $t = 0$, due to a mols of cane sugar, let α_0' denote the angle of rotation, when inversion is complete, and let α be the angle of rotation at any time t; then, since rotation of the plane of polarization is proportional to the concentration x, the amount of cane sugar inverted, will be

$$x = a\frac{\alpha_0 - \alpha}{\alpha_0 + \alpha_0'}.$$

In the equation,

$$C_{12}H_{22}O_{11} + H_2O \rightleftarrows C_6H_{12}O_6 + C_6H_{12}O_6,$$

representing the inversion of cane sugar, the velocity of the reaction, according to the law of mass action, will be proportional to the molecular concentrations of the cane sugar and the water. Since the reaction takes place in the presence of such a large excess of water, its effect may be considered to be constant. The velocity of the reaction is then proportional to the active mass of the sugar alone, or in other words, the reaction is unimolecular. In the differential equation, expressing the velocity of a unimolecular reaction,

$$\frac{dx}{dt} = k\,(a - x),$$

we have

$$k = \frac{1}{t}\log_e\frac{a}{a - x};$$

and, since a and x are measured in terms of angles of rotation of the plane of polarization, we have

$$k = \frac{1}{t} \log_e \frac{\alpha_0 + \alpha_0'}{\alpha + \alpha_0'}. \tag{11}$$

The following table gives the results obtained with a 20 per cent solution of cane sugar in the presence of a 0.5 molar solution of lactic acid at 25° C.

HYDROLYSIS OF CANE SUGAR

t (minutes).	α	$k \times 10^{-4}$
0	34°.5	.....
1,435	31°.1	0.2348
4,315	25°.0	0.2359
7,070	20°.16	0.2343
11,360	13°.98	0.2310
14,170	10°.01	0.2301
16,935	7°.57	0.2316
19,815	5°.08	0.2291
29,925	− 1°.65	0.2330
Inf.	−10°.77	.....

Bimolecular Reactions. When a reaction depends on the collision between two molecules (either of the same or different species) the reaction is *bimolecular, or a reaction of the second order.* Let a and b represent the initial molar concentrations of the two reacting substances, and let x denote the amount transformed in the interval of time t; then the velocity of the reaction will be expressed by the equation,

$$\frac{dx}{dt} = k\,(a - x)\,(b - x) \tag{12}$$

The simplest case is that in which the two substances are present in equivalent amounts. Under these conditions, the velocity equation becomes

$$\frac{dx}{dt} = k\,(a - x)^2. \tag{13}$$

Integrating equation (13), we have

$$k = \frac{1}{t} \cdot \frac{x}{a\,(a - x)}. \tag{14}$$

If the reacting substances are not present in equivalent amounts, then we must employ the equation

$$\frac{dx}{dt} = k\,(a - x)\,(b - x).$$

On integration, this becomes

$$kt = \frac{1}{a - b} \log_e \frac{b\,(a - x)}{a\,(b - x)}. \tag{15}$$

Or, passing to Briggsian logarithms,

$$0.4343\,k = \frac{1}{t\,(a - b)} \log \frac{b\,(a - x)}{a\,(b - x)}. \tag{16}$$

The value of k, in a bimolecular reaction, is not independent of the units in which the concentration is expressed, as is the case with a unimolecular reaction. Suppose that a unit 1/nth of that originally selected is used to express concentration, then the value of k in the equation,

$$k = \frac{1}{t} \frac{x}{a\,(a - x)},$$

becomes

$$k' = \frac{1}{t} \cdot \frac{nx}{na \cdot n\,(a - x)} = \frac{1}{t} \cdot \frac{x}{na\,(a - x)}.$$

Thus, the value of k varies inversely as the numbers expressing the concentrations.

As an illustration of a bimolecular reaction, we may take the hydrolysis of an ester by an alkali. The reaction,

$$CH_3COOC_2H_5 + NaOH \rightleftarrows CH_3COONa + C_2H_5OH,$$

has been studied by Warder,* Reicher,† Arrhenius,‡ Ostwald § and others. Arrhenius employed, in his experiments, 0.02 molar solutions of ester and alkali. These solutions were placed in separate flasks, and warmed to 25° C. in a thermostat maintained at that temperature; equal volumes were then mixed and, at

* Berichte, 14, 1361 (1881).
† Lieb. Ann., 228, 257 (1885).
‡ Zeit. phys. Chem., 1, 110 (1887).
§ Jour. prakt. Chem., 35, 112 (1887).

frequent intervals, a portion of the reaction mixture was removed and titrated rapidly with standard acid. The accompanying table contains some of the results obtained:

HYDROLYSIS OF ETHYL ACETATE

t (minutes).	$a - x$	k
0	8.04	.....
4	5.30	0.0160
6	4.58	0.0156
8	3.91	0.0164
10	3.51	0.0160
12	3.12	0.0162
		Mean 0.0160

The numbers in the second column of the table represent the concentrations of sodium hydroxide and of ethyl acetate, expressed in terms of the number of cubic centimeters of standard acid required to neutralize 10 cc. of the reaction mixture. Owing to the high velocity of the reaction, it is difficult to avoid large experimental errors, nevertheless, the values of k, given in the third column of the table, will be observed to differ very slightly from the mean value.

Reicher investigated the same reaction, when the reacting substances were not present in equivalent proportions. In this case, the progress of the reaction was followed by titrating definite portions of the reaction mixture, from time to time, the excess of sodium hydroxide being determined by titrating a portion of the mixture at the expiration of twenty-four hours, when the ester was completely hydrolyzed. His results are given in the following table:

HYDROLYSIS OF ETHYL ACETATE

t (minutes).	$a - x$ (alkali).	$b - x$ (ester).	k
0	61.95	47.03	.....
4.89	50.59	35.67	0.00093
11.36	42.40	27.48	0.00094
29.18	29.35	14.43	0.00092
Inf.	14.92	0	.....

Reicher also studied the effect of different bases upon the velocity of the reaction. He found, for strong bases, approximately equal values of k, but for weak bases, the values were irregular and smaller than those obtained with the more completely ionized bases. Arrhenius pointed out, that the hydrolyzing power of a base is proportional to the number of hydroxyl ions which it yields. Writing the equation for the above hydrolysis in terms of ions, we have

$$CH_3COOC_2H_5 + Na^{\cdot} + OH' \rightleftarrows CH_3COO' + Na^{\cdot} + C_2H_5OH.$$

It is evident from this equation, that all bases furnishing the same number of hydroxyl ions should give identical values of k. Therefore, we may modify the fundamental differential equation as follows:

$$\frac{dx}{dt} = k'\alpha\,(a - x)\,(b - x), \tag{17}$$

where α is the degree of ionization of the base.

Trimolecular Reactions. Any reaction in which three reacting molecules are directly involved is *trimolecular, or of the third order.* If the initial molar concentrations of the reacting substances are denoted by a, b, and c, and if x denotes the concentration of each which is transformed in the interval of time t, the velocity of the reaction will be represented by the differential equation,

$$\frac{dx}{dt} = k\,(a - x)\,(b - x)\,(c - x). \tag{18}$$

If the substances are present in equivalent amounts, the equation becomes

$$\frac{dx}{dt} = k\,(a - x)^3, \tag{19}$$

an expression which is much less difficult to integrate.

On integration, equation (19) becomes

$$k = \frac{1}{t} \cdot \frac{x\,(2\,a - x)}{2\,a^2\,(a - x)^2}. \tag{20}$$

When the reacting substances are not taken in equivalent amounts, the integration of the velocity equation gives,

$$k = \frac{1}{t} \cdot \frac{\log_e\left(\frac{a - x}{a}\right)^{(b-c)} \cdot \log_e\left(\frac{b - x}{b}\right)^{(c-a)} \cdot \log_e\left(\frac{c - x}{c}\right)^{(a-b)}}{(a - b)\,(b - c)\,(c - a)}. \tag{21}$$

In a trimolecular reaction, k is inversely proportional to the square of the original concentration.

A typical trimolecular reaction is that between ferric and stannous chlorides. This reaction, represented by the following equation

$$2\,FeCl_3 + SnCl_2 \rightleftarrows 2\,FeCl_2 + SnCl_4,$$

has been investigated by A. A. Noyes.* Dilute solutions of the reacting substances were mixed at constant temperature, and definite portions of the reaction mixture were removed, at measured intervals of time, and titrated for ferrous iron. Before titrating with a standard solution of potassium permanganate, it was necessary to decompose the stannous chloride present with mercuric chloride. The following table gives the results obtained with 0.025 normal solutions of ferric chloride and stannous chloride

REDUCTION OF $FeCl_3$ BY $SnCl_2$

t (minutes).	$a - x$	x	k
2.5	0.02149	0.00351	113
3	0.02112	0.00388	107
6	0.01837	0.00663	114
11	0.01554	0.00946	116
15	0.01394	0.01106	118
18	0.01313	0.01187	117
30	0.01060	0.01440	122
60	0.00784	0.01716	122
			Mean 116

Noyes also found, that the velocity of the reaction is accelerated more by an excess of ferric chloride than by an equal excess of stannous chloride.

Reactions of Higher Orders. Reactions of the fourth, fifth and eighth orders, have recently been investigated, but examples of reactions of orders higher than the third are extremely rare. This fact is at first sight surprising, since the equations of many chemical reactions involve a large number of molecules, and we should naturally expect a corresponding increase in the order of such reactions. For example, the reaction represented by the equation,

$$2\,PH_3 + 4\,O_2 = P_2O_5 + 3\,H_2O,$$

* Zeit. phys. Chem., 16, 546 (1895).

involves six molecules of the substances initially present, and therefore, we should infer it to be a reaction of the sixth order. Kinetic experiments by van der Stadt, have shown it to be a bimolecular reaction, the velocity of reaction being proportional to the concentrations of the phosphine and the oxygen. On allowing the gases to mix slowly by diffusion, it was discovered, that the reaction actually takes place in several successive stages, the first stage being represented by the equation of the bimolecular reaction,

$$PH_3 + O_2 = HPO_2 + H_2.$$

The subsequent changes, involving the oxidation of the products of this reaction, take place with great rapidity.

It is highly probable, that the equations which are ordinarily employed to represent chemical reactions, really represent only the initial and final stages of a series of relatively simple reactions. Larmor * has shown, that when chemical reactions are considered from the molecular standpoint, the bimolecular reaction is the most probable. He says, " Imagine a substance, say gaseous for simplicity, formed by the immediate spontaneous combination of three gaseous components A, B, and C. When these gases are mixed, the chances are very remote of the occurrence of the simultaneous triple encounter of an A, a B, and a C, which would be necessary to the immediate formation of an ABC; whereas, if ever formed, it would be liable to the normal chance of dissociating by collisions; it would thus be practically non-existent in the statistical sense. But if an intermediate combination, AB, could exist, very transiently, though long enough to cover a considerable fraction of the mean free path of the molecules, this will readily be formed by ordinary binary encounters of A and B, and another binary encounter of AB with C will now form the triple compound ABC in quantity."

Determination of the Order of a Reaction. It has been shown in the foregoing pages, that the time required to complete a certain fraction of a reaction is dependent upon the order of the reaction in the following manner:

(1) In a unimolecular reaction, the value of k is independent of the initial concentration;

(2) In a bimolecular reaction, the value of k is inversely proportional to the initial concentration;

* Proc. Manchester Phil. Soc., 1908.

(3) In a trimolecular reaction, the value of k is inversely proportional to the square of the initial concentration.

Hence, in general, in a reaction of the nth order, the value of k is inversely proportional to the $(n - 1)$ power of the initial concentration. If the value of k is determined with definite concentrations of the reacting substances, and then with multiples of those concentrations, the order of the reaction can be determined, according to the above rules, by observing the manner in which k varies with the concentration.

The order of a reaction may also be readily determined by means of a graphic method. Thus, to determine the order of a reaction, we ascertain by actual trial which one of the following expressions, in which C denotes concentration (at time t), will give a straight line when plotted against times as abscissæ:

(1) $\log C$ — reaction unimolecular;
(2) $1/C$ — reaction bimolecular;
(3) $1/C^2$ — reaction trimolecular;
(4) $1/C^n$ — reaction $n + 1$ molecular.

Complex Reaction Velocities. Thus far we have considered the velocity of reactions which are practically complete. There are numerous cases, however, in which the course of the reaction is complicated by such disturbing factors, as (1) *counter reactions*, (2) *side reactions*, and (3) *consecutive reactions*. These disturbing causes will now be considered.

(1) *Counter Reactions.* In the chemical change represented by the equation,

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

the speed of the direct reaction steadily diminishes, owing to the ever-increasing effect of the reverse, or counter reaction. Ultimately, when two-thirds of the acid and alcohol are decomposed, the velocities of the two reactions become equal, and a condition of equilibrium results. Starting with 1 mol of acid and 1 mol of alcohol, and letting x represent the amount of ester formed, we have

$$\frac{dx}{dt} = k(1 - x)^2 - k'x^2. \qquad (22)$$

When equilibrium is attained,

$$K_c = \frac{k}{k'} = 4.$$

By observing the change for any time t, we have

$$k - k' = \frac{3}{4t} \log_e \frac{2 - x}{2 - 3x}. \tag{23}$$

Having the values of k/k', and $k - k'$, the velocity constant, k, of the direct reaction can be determined. The value of k, so obtained, has been shown by Knoblauch * to vary in those reactions where the concentration of the hydrogen ion changes.

(2) *Side Reactions.* When the same substances are capable of reacting in more than one way, with the formation of different products, the several reactions proceed side by side. Thus, benzene and chlorine may react in two ways, as shown by the equations,

$$(1)\ C_6H_6 + Cl_2 = C_6H_5Cl + HCl,$$

and

$$(2)\ C_6H_6 + 3\,Cl_2 = C_6H_6Cl_6.$$

It is generally possible to regulate the conditions under which the substances react, so as to promote one reaction and retard the other.

(3) *Consecutive Reactions.* By consecutive reactions, we understand those reactions, in which the products of a certain initial chemical change, react, either with each other, or with the original substances, to form new substances. Attention has already been called to the fact, that many of our common chemical equations really represent the summation of a number of consecutive reactions. If the system A, is transformed into the system C, through an intermediate system B, then we shall have the two reactions,

$$(1)\quad A \rightarrow B,$$

and

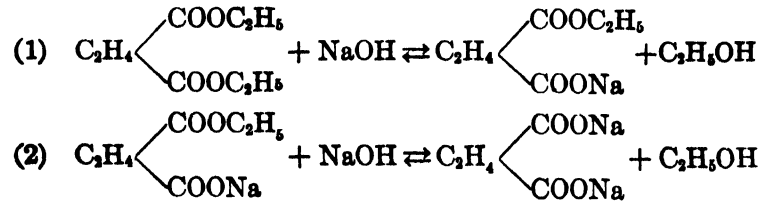
$$(2)\quad B \rightarrow C.$$

If reaction (1) should have a very much greater velocity than reaction (2), then, the measured velocity of the change from A to C, will be practically the same as that of the slower reaction. This fact has been illustrated by means of the following analogy, due to James Walker: — † " The time occupied by the transmission of a telegraphic message depends both on the rate

* Zeit. phys. Chem., 22, 268 (1897).

† Proc. Roy. Soc., Edinburgh, 22 (1898).

of transmission along the conducting wire, and on the rate of progress of the messenger who delivers the telegram; but, it is obviously this last slower rate, that is of really practical importance in determining the time of transmission." The saponification of ethyl succinate may be taken as an illustration of consecutive reactions. This reaction proceeds in two stages as follows:



In this case, the product of the first reaction reacts with one of the original substances.

Velocity of Heterogeneous Reactions. It has been shown, that when a solid, such as calcium carbonate, is dissolved in an acid, the rate of solution is dependent upon the surface of contact between the solid and liquid phases, and also upon the strength of the acid. If the surface is large so that it undergoes relatively little change during the reaction, it may be considered as constant. If S represents the area of the surface exposed, and x denotes the amount of solid dissolved in the time t, the velocity of the reaction will be represented by the differential equation,

$$\frac{dx}{dt} = kS\,(a - x). \tag{24}$$

Integrating this equation, we have

$$kS = \frac{1}{t}\log_e \frac{a}{a - x}. \tag{25}$$

This formula has been tested by Boguski * for the reaction,

$$CaCO_3 + 2\,HCl = CaCl_2 + CO_2 + H_2O,$$

and is found to give constant values of k. Furthermore, Noyes and Whitney † have shown, that the rate of solution of a solid in a liquid at any instant, is proportional to the difference between the concentration of the saturated solution and the concentration of the solution at the time of the experiment.

* Berichte, 9, 1646 (1876).

† Zeit. phys. Chem., 23, 689 (1897).

Velocity of Reaction and Temperature. It is a well-established fact, that the velocity of a chemical reaction is accelerated by rise of temperature. Thus, the rate of inversion of cane sugar is increased about five times, for a rise in temperature of 30°. It has been shown, as the result of a large number of observations on a variety of chemical reactions, that in general the velocity of a reaction is doubled, or trebled, for an increase in temperature of 10°. It is of interest to note, that the rate of development of various organisms, such as yeast cells, the rate of growth of the eggs of certain fishes, and the rate of germination of certain varieties of seeds, is either doubled, or trebled, for a rise in temperature of 10°. Up to the present time, no wholly satisfactory formula, connecting the rate of reaction with the temperature has been derived, although several purely empirical expressions have been suggested. Of these formulas, the most widely applicable is that proposed by van't Hoff, and verified by Arrhenius. If k_0 and k_1 represent the velocity constants at the respective temperatures, T_0 and T_1, then

$$k_1 = k_0 e^{\left(\frac{A\,(T_1 - T_0)}{T_0 T_1}\right)} \tag{26}$$

where e is the base of the Naperian system of logarithms, and A is a constant. The following table gives the calculated and observed values of k, at various temperatures, for the reaction,

$$NH_4CNO \rightleftarrows OC\begin{matrix}NH_2\\ \diagdown\\ \diagup\\ NH_2\end{matrix}$$

when $T = 273 + 25°$, $k = 0.000227$, and $A = 11{,}700$.

VARIATION OF VELOCITY CONSTANT WITH TEMPERATURE

T, Degrees	k (observed)	k (calculated)
273 + 39	0.00141	0.00133
273 + 50.1	0.00520	0.00480
273 + 64.5	0.0228	0.0227
273 + 74.7	0.062	0.0623
273 + 80	0.100	0.105

In this case, the agreement between the observed and calculated values is all that could be desired.

Influence of the Solvent on the Velocity of Reaction. The velocity of a chemical reaction varies greatly with the nature of the medium in which it takes place. This subject has been studied by Menschutkin,* who has collected valuable data, as the result of a large number of experiments, on the velocity of the reaction between ethyl iodide and triethylamine, as represented by the equation,

$$C_2H_5I + (C_2H_5)_3N = (C_2H_5)_4NI.$$

This reaction was allowed to take place in a large number of different solvents, and the velocity at 100° was measured. A few of Menschutkin's results are given in the accompanying table, in which k denotes the velocity constant.

VARIATION OF VELOCITY CONSTANT WITH REACTION MEDIUM

Medium.	k	Medium.	k
Hexane	0.00018	Ethyl alcohol	0.0366
Ethyl ether	0.000757	Methyl alcohol	0.0516
Benzene	0.00584	Acetone	0.0608

These figures show that the velocity of the reaction is greatly modified by the nature of the medium in which it takes place, the velocity in hexane being less than one three-hundredth of that in acetone.

The influence of the solvent on the velocity of reaction has been further investigated by von Halban† who studied the rate of decomposition of triethylsulphine bromide into diethyl sulphide and ethyl bromide, the reaction being represented by the equation,

$$(C_2H_5)_3SBr = (C_2H_5)_2S + C_2H_5Br.$$

The reaction was carried out in a number of organic solvents at different temperatures. The solvents, as regards their effect on the rate of the reaction, were found to divide themselves into two classes, as follows: (1) Those containing hydroxyl groups, such as the alcohols and acetic acid, in which the velocity is small,

* Zeit. phys. Chem., 6, 41 (1890).
† Ibid., 67, 129 (1909).

and (2) other solvents, such as acetone and chloroform, in which the velocity is relatively high. The variation of velocity within the groups was found to be comparatively small. The temperature coefficient of the reaction was found to be high, the value for a change of 10° C. being in some cases as high as 6, at low temperatures. In almost every case the variation of the velocity of the reaction with temperature was found to be satisfactorily represented by the formula of Arrhenius, as given in the preceding section. No general relationship was found to exist between the rate of reaction and the properties of the solvent. This is contrary to the statement of Menschutkin that there is a parallelism between the values of the velocity constant and the dielectric constants of the solvent media.

Catalysis. It is a familiar fact, that the velocity of a chemical reaction is frequently greatly accelerated by the presence of a foreign substance which apparently does not participate in the reaction, and which remains unchanged when the reaction is complete. For example, cane sugar is inverted very slowly by pure water alone, but when a trace of acid is added, the reaction is greatly accelerated. A substance which is capable of exerting such an accelerating action is termed a *catalyst*, and the process is known as *catalysis*. Ostwald likens the action of a catalyst to that of a lubricant on a machine, — it helps to overcome the resistance of the reaction. According to this point of view, a catalyst is not strictly essential but merely hastens a reaction which would otherwise proceed at a much slower rate. On the other hand, there are those who contend that the catalyst is essential and that without it reaction could not take place. These two points of view have been likened to a game in which the catalyst is either comparable to the crowd which cheers the players, or is looked upon as an essential player without whom the game could not progress.

A catalyst has been defined by Ostwald, as "an agent which affects the velocity of a chemical reaction without appearing in the final products of the reaction." While this definition is perhaps incomplete, nevertheless, it embodies the outstanding characteristics of catalytic action.

The Criteria of Catalysis. The following criteria characterize chemical reactions in which catalysis plays an important part.

(1) *Positive and Negative Catalysis.* According to Ostwald's definition, a catalytic agent may exert a retarding, as well as an

accelerating, influence on the velocity of a chemical reaction. A catalyst which exerts an accelerating influence is known as a *positive catalyst*, whereas a catalyst which exerts a retarding influence is called a *negative catalyst*. While practically all catalysts are positive in their action, there are a few which are known to exert an opposite influence. Thus, Bigelow* has found that the rate of oxidation of sodium sulphite is retarded by the presence in the solution of as little as one one-hundred-and-sixty-thousandth of a mol of mannite per liter.

(2) *Unalterability of the Catalyst.* While a catalyst may actually participate in a chemical reaction, it will reappear at the end of the reaction, unaltered both in chemical composition and in amount. This is undoubtedly the most striking characteristic of all catalytic agents. In this connection, it should be stated, that notwithstanding the fact that the chemical composition of a catalyst remains unchanged, it quite often happens that its *physical* condition undergoes marked alteration. In fact, many catalysts do not attain to their maximum efficiency until such alteration, or " ageing," has occurred.

(3) *Amount of Catalyst Required.* The amount of catalyst required to promote the transformation of a large mass of reacting material is generally exceedingly small. The amount of catalyst also remains constant, unless interfering side-reactions take place. In certain cases, the amount of catalyst is found to increase as the reaction proceeds, while in other cases, the amount of catalyst is found to decrease. This has been shown to be due to the fact, that the catalyst is actually being formed, or absorbed, as the reaction proceeds. Thus, when metallic copper is dissolved in nitric acid, the reaction proceeds, slowly at first, and then after a short interval, the speed of the reaction is greatly augmented. The acceleration is due to the catalytic action of the nitric oxide evolved. This phenomenon is known as *autocatalysis*. In reactions where autocatalysis occurs, the velocity increases with the time, until a certain maximum value is reached, after which, the velocity steadily diminishes. In ordinary reactions, the initial velocity is the greatest.

As a generalization, to which there are numerous exceptions, it may be stated that reaction velocity is approximately proportional to the amount of catalyst present.

* Zeit. phys. Chem., **26**, 493 (1898).

(4) *Rôle of Catalyst in Initiating Reaction.* As to whether, or not, a catalyst is capable of initiating a chemical reaction, it is difficult to decide. Take, for example, the reaction between hydrogen and oxygen, which does not appear to take place at all under ordinary conditions of temperature, unless some catalyst, such as finely divided platinum, is present. Ostwald contends, that the reaction actually occurs at ordinary temperatures, but that the velocity is too small to admit of measurement. Others maintain, that no reaction occurs under these conditions, and that the introduction of a catalyst is necessary in order to initiate the combination of the two gases.

(5) *Influence of Catalyst upon Equilibrium.* As we have seen, the final state of equilibrium in a chemical reaction depends solely on the ratio of the velocities of the direct and inverse reactions. Since this equilibrium is not disturbed by the introduction of a catalyst, it follows, that the velocities of the two reactions must be altered to the same extent. Furthermore, the amount of energy transformed in a chemical reaction, represents the difference between the amounts of energy stored in the system in its initial and final states. Since the catalyst introduces no energy, it is evident, that it cannot exert any influence on the final state of equilibrium.

(6) *Influence of Foreign Substances on Catalyst.* The activity of a catalyst is appreciably altered by the presence of extremely minute amounts of foreign substances. In some instances, the activity is diminished, and in others, it is increased. Foreign substances which tend to inhibit catalytic activity are known as *poisons*, while substances which tend to enhance the activity are called *promoters*. The presence of the merest trace of a poison is often sufficient to cause the complete paralysis of a catalyst. For example, in the manufacture of sulphuric acid by the familiar contact process, the presence of a very minute amount of arsenic in the sulphur dioxide has been found sufficient to destroy completely the activity of the platinum-asbestos catalyst. On the other hand, the mixture of minute amounts of certain promoters, such as finely divided oxides, with practically any of the ordinary metallic catalysts, is found greatly to enhance their activity. Thus, in the Haber process for the synthesis of ammonia from its elements, the addition of a trace of certain metallic salts to the finely divided iron used as a catalyst, produces an enormous increase in its activity.

(7) *Specificity of Catalytic Action.* While it is probable that every chemical reaction is more or less susceptible to catalytic influence, and also that practically every known substance is capable of functioning as a catalyst, nevertheless, it is certain that each reaction requires a particular catalyst, or group of catalysts, to modify its velocity. In other words, catalytic activity appears to be specific.

Theories of Catalysis. The various alternative theories which have been advanced from time to time in explanation of the mechanism of catalytic action may conveniently be considered under the three following headings: (1) Intermediate Compound Theory; (2) Adsorption Theory, and (3) Electrochemical Theory.

(1) *Intermediate Compound Theory.* Of the many explanations which have been offered to account for catalytic acceleration, that involving the formation of hypothetical intermediate compounds with the catalyst has perhaps been accepted with the greatest favor. Thus, if a reaction represented by the equation,

$$A + B = AB,$$

takes place very slowly under ordinary conditions, it is possible to accelerate its velocity by the addition of an appropriate catalyst, C. According to the theory of intermediate compounds, the catalyst is supposed to act in the following manner:

$$(1) \quad A + C = AC,$$
$$(2) \quad AC + B = AB + C.$$

As will be seen, the catalyst is regenerated in the second stage of the reaction. A catalyst which functions in this manner is known as a *Carrier.* In 1806, Clement and Desormes* suggested that the action of nitric oxide in promoting the oxidation of sulphur dioxide, in the manufacture of sulphuric acid, was purely catalytic. As is well known, the rate of the reaction represented by the equation,

$$2\,SO_2 + O_2 = 2\,SO_3,$$

is very slow. The accelerating action of nitric oxide on the reaction may be represented in the following manner:

$$(1) \quad 2\,NO + O_2 = 2\,NO_2,$$

and

$$(2) \quad SO_2 + NO_2 = SO_3 + NO.$$

* Clement and Desormes, Ann. Chim., 59, 329 (1806).

This explanation, first offered by Clement and Desormes, of the part played by the oxides of nitrogen in the synthesis of sulphuric acid, is still regarded as the most plausible, although it is apparent that it is far from complete.

Visible evidence of intermediate compound formation is afforded by the reaction in which formaldehyde is produced as the result of the fractional combustion of methyl alcohol by air at low temperatures, copper gauze being employed as a catalyst. As the reaction proceeds, the surface of the gauze changes color, due to the alternate reduction and oxidation of one of the oxides of copper. CuO, Cu_2O or Cu_4O.

As the result of investigations extending over a period of many years, Sabatier* has concluded that the most satisfactory explanation of the behavior of nickel as a catalyst, in hydrogenation processes, is that involving the formation of an unstable hydride of nickel.

Numerous examples in support of the intermediate compound theory are found in the realm of organic chemistry. Probably the most familiar of these is the preparation of ether from alcohol, using sulphuric acid as the catalytic agent. That an intermediate compound is actually formed in this reaction was first proven by Williamson who detected the presence of sulphovinic acid in the reaction mixture.

(2) *Adsorption Theory.* This interesting and suggestive theory was first proposed by Faraday to explain the remarkable catalytic activity of platinum in accelerating the combination of hydrogen with oxygen. He concluded that the proximity of the particles of the reacting gases to the surface of the platinum must be comparable to that which would obtain were the gases condensed to the liquid state.

In other words, he believed the gaseous particles to be much closer to the metal surface than they are to each other in the body of the gaseous mixture. He also showed that the power of platinum to induce combination between hydrogen and oxygen depends not only upon the previous treatment of the metallic surface, but also upon the absence of exceedingly minute traces of certain gases, such as carbon monoxide.

The concept of surface condensation, or adsorption, as the cause of catalytic action, as originally put forward by Faraday, has been

* Sabatier, La Catalyse en Chimie Organique.

adopted, with modifications, by J. J. Thomson,* Bone,† Langmuir,‡ and numerous other investigators. From the study of the behavior of tungsten filaments heated to high temperatures in the presence of traces of oxygen at low pressures, Langmuir has shown that the metallic filament is practically completely covered with a film of oxygen, the thickness of which is of the order, 1×10^{-8} cm. The remarkable stability of these oxygen films, as well as the complete change in the chemical properties of the gas, is adduced as evidence in favor of the existence of an adsorbed layer of oxygen atoms on the surface of the tungsten. Langmuir points out that this film cannot be regarded as an oxide of tungsten, nor as atomic oxygen, in the sense in which we ordinarily regard free oxygen atoms. The oxygen atoms, he contends, are probably held to the surface of the metal by four pairs of electrons, just as the oxygen atom is held to the carbon atom in carbon dioxide. While the oxygen atoms are thus chemically saturated, the tungsten atoms remain unsaturated and are held by strong attractive forces to the tungsten atoms which lie immediately below them. This view is in accord with the modern conception of the structure of solids as revealed by X-ray analysis. There is an abundance of experimental evidence in support of the view that stable films also exist at atmospheric pressure, quite analogous to those observed in high vacua and at high temperatures.

According to Langmuir, the clean surface of a solid crystalline body must consist of atoms, or molecules, arranged in a surface-lattice, or kind of checkerboard. Non-crystalline bodies, such as glass, must have surfaces in which the atoms are probably not in regular lattices. We may also have surfaces which are porous, or consist of irregular filamentary projections and interlocking chains of atoms, or molecules. In such cases the extent of surface cannot be defined, except in a purely arbitrary manner. Most finely divided catalysts such as platinum black, or activated charcoal, must have structures of great complexity, and it is probable that the atoms are attached to each other in the form of branching chains, so that there are hardly any small groups of atoms which are as closely packed as they would be in a crystalline solid. In general, we should look upon the surface of a catalyst as consisting

* J. J. Thomson, Applications of Dynamics to Physics and Chemistry.

† Bone, Jour. Chem. Soc., 81, 538 (1902).

‡ Langmuir, Trans. Faraday Soc., 17, 607 (1922).

of a checkerboard in which some of the spaces are vacant, while others are filled with atoms, or molecules. Some of these molecules, or atoms, may be so firmly attached that they do not evaporate at an appreciable rate. Others leave the surface from time to time, and the vacant spaces thus left are sooner or later filled by other molecules which strike the surface and condense.

It is highly probable that in the adsorbed layer the molecules are more or less oriented. Reference has already been made in a preceding chapter (see p. 306) to the experiments of Langmuir and Harkins on the spreading of oils on the surface of water in which it was shown that the molecules on the surface are oriented, the actual surface consisting of the hydrocarbon portion of the molecules, while the polar or active groups, such as the carboxyl or hydroxyl groups, are directed inwards towards the water.

Evidence that surface films are oriented is also obtained from surface tension data on pure liquids, and calculation shows these films to be monomolecular. It follows, therefore, that molecular orientation probably is involved in all adsorption phenomena and, likewise, in all surface catalytic actions.

(3) *Electrochemical Theory.* There is an abundance of experimental evidence in favor of the view that at all adsorption boundaries there exists a so-called "electrical double layer." Such a condition can only be established by the electrical orientation of a layer of neutral molecules, or in the case of an electrolyte, of selective adsorption of one of the ions of the electrolyte, with the simultaneous formation of a layer of oppositely charged ions held to the surface of the adsorbent by electrostatic attraction. The electrochemical theory of catalysis may be regarded as a modification of the adsorption theory, in which the catalytic agent is directive as well as selective in its action. In fact, the hypothesis of a distinct directive force necessitates the existence of some form of union between the surface of the catalyst and the molecules of the reaction mixture. Such quasi-chemical combinations may, in the limiting case, be regarded as definite intermediate compounds.

In reviewing the numerous investigations of catalytic phenomena which have been conducted within the past few years, Taylor* writes,

"In so far as the contact agent itself is concerned, these researches have supplied a consistent, intelligible picture of its nature and of its special

* Taylor, Jour. Phys. Chem., 30, 171 (1926).

properties. This picture supplies a reason for much of the mystery with which the subject of contact catalysis has been surrounded hitherto. For, it shows that the properties of the contact agent are to be differentiated from the bulk properties of the substance of which the catalyst is composed; that it is rather the properties of the individual atoms or molecules of the catalyst, with the changes in these properties induced by position and arrangement in the catalyst particle, which are of importance in catalytic change. The ordinary general, inorganic, and organic chemistry of substances is concerned with the reactions and properties of many million millions of examples of such atoms or molecules, and the result given is the statistical average covering all the cases. The properties of the contact agent, especially in catalytic reactions difficultly achieved, are those of the aristocracy of the atomic or molecular species concerned, and are as different from the statistical average behavior of the crowd as the actions of an educated minority of people should be different from that of an indiscriminately collected mob."

Catalytic Action of Water. Water, seemingly, functions as a catalyst in a large number of chemical reactions. Thus, it has been shown by Baker* that no reaction occurs when hydrochloric acid and ammonia are brought together in a perfectly dry condition, but that when a minute trace of water is introduced, the reaction proceeds rapidly to completion.

Other examples of gases which show no tendency to combine, except when a trace of water is present, are nitric oxide and oxygen, cyanogen and oxygen, hydrogen and chlorine, and ammonia and carbon dioxide. Baker has also shown that a number of substances which ordinarily are appreciably dissociated, when moist and in the vapor state, fail to dissociate when perfectly dry. Thus, ammonium chloride, nitrogen peroxide, phosphorus pentachloride and mercurous chloride, if completely dry, remain undissociated when heated.

Quite recently, Baker† has shown that when a series of carefully purified liquids were subjected to thorough drying over a period of from eight to nine years, their boiling points increased from 14° to 62° above the boiling points of the same liquids as ordinarily dried.

It has been suggested by Smits‡ that the inactivation of substances by prolonged drying may be ascribed to the existence of two types of molecules, the equilibrium between which is dis-

* Baker, Jour. Chem. Soc., 65, 611 (1894); 77, 646 (1900); 91, 1862 (1907).
† Baker, ibid., 121, 568 (1922); 123, 1223 (1923).
‡ Smits, Proc. Acad. Sci. Amsterdam, 26, No. 3 (1923).

placed during the drying process in the direction of the less active type. While this explanation of the remarkable results obtained by Baker is in some ways satisfactory, yet, as Lewis* has pointed out, it seems more rational to attribute the change in properties of the dried liquids to the absence of water. In support of this view he cites the fact that ammonia, which in many respects resembles water, functions as a catalyst in the transformation of λ-sulphur into μ-sulphur, while in the absence of ammonia the two forms remain unchanged.

Some Applications of Catalysis. A few of the many applications of catalysis in the realm of industrial chemistry should be briefly mentioned, in order that the great practical importance of this interesting subject may receive sufficient emphasis.

(1) *The Deacon Process.* In 1888, Deacon and Hurter, by passing a mixture of hydrochloric acid gas and oxygen over pumice, impregnated with cupric chloride as a catalyst, showed that the velocity of the reaction,

$$4\,HCl + O_2 = 2\,H_2O + 2\,Cl_2,$$

can be sufficiently accelerated to render its employment entirely practicable in the production of chlorine on the commercial scale. The catalyst is very sensitive to such poisons as sulphur dioxide, sulphur trioxide and arsenic. Water also has been found to interfere with the reaction, so that it is necessary that the two gases shall be thoroughly dried before being allowed to enter the reaction chamber.

(2) *The Haber Process.* Although the affinity of nitrogen for hydrogen is known to be so feeble that, at the temperature of the electric spark, and under atmospheric pressure, practically no ammonia is formed, yet by a careful study of the conditions governing the equilibrium represented by the equation,

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3,$$

and by the employment of proper catalytic agents, Haber succeeded in producing ammonia on a commercial scale by means of this reaction. At 1000°, ammonia may be regarded as completely dissociated, while at 550°, and under atmospheric pressure, only

* Lewis, Jour. Am. Chem. Soc., 45, 2836 (1923).

about 0.08 per cent of ammonia is formed. Increase of pressure, however, displaces the equilibrium, in accordance with the principle of Le Chatelier, so that more of the system occupying the smaller volume, namely ammonia, is formed. Thus, at 550°, and under a pressure of 200 atmospheres, the amount of ammonia formed is nearly 12 per cent. Despite the fact that this percentage is so small, this amount of ammonia can be removed as ammonia of crystallization by ammonium nitrate, at a low temperature, and fresh portions of hydrogen and nitrogen introduced into the reaction chamber, thus rendering the process continuous. Various catalysts have been employed, but pure iron appears to be the most efficient. With this catalyst and suitable promoters, it is claimed that the process can be conducted efficiently at pressures as low as 50 atmospheres. Here again, the catalyst is very susceptible to the presence of poisons such as sulphur, selenium, tellurium, arsenic, etc. It is stated that 0.01 per cent of sulphur is sufficient to destroy completely the catalytic activity of the iron catalyst. The Haber process played an important part in providing Germany with fixed nitrogen during the recent war.

(3) *Sabatier's Hydrogenation Process.* Toward the latter part of the nineteenth century, Sabatier and Senderens* discovered that reduced nickel will bring about the combination of hydrogen with ethylene, or acetylene, with the formation of ethane, as shown by the equations,

$$C_2H_4 + H_2 = C_2H_6,$$
$$C_2H_2 + 2\,H_2 = C_2H_6.$$

In this method of hydrogenation, the vapor of the substance to be reduced is mixed with hydrogen and passed over a specific catalyst, which is maintained at a temperature ranging from 150° to 300°. The process is not only extremely rapid, but also requires a minimum amount of attention. Furthermore, the yields are relatively high, provided proper care is taken to maintain the temperature within the prescribed limits necessary to minimize the formation of subsidiary products. Although nickel is the most efficient catalyst, other metals, such as cobalt, platinum, iron and copper, may be used. Whatever catalyst is employed.

* Compt. rend., 124, 1358 (1897); 128, 1173 (1899).

it is absolutely essential that great care be taken in its preparation, since the success of the method is largely dependent upon the condition of the metal. The catalyst is very susceptible to various poisons, particularly chlorine, sulphur, arsenic and phosphorus and their compounds.

The process has found numerous applications, notably in the preparation of artificial perfumes. It also has proven of value in the synthesis of cyclohexanol and p-methylcyclohexanol, from phenol and p-cresol, respectively. Both of these substances are used in the preparation of isoprene and butadiene, compounds of importance in connection with the synthesis of artificial rubber. Undoubtedly the most important industrial application of the hydrogenation process is in the conversion of unsaturated aliphatic acids, such as oleic acid, into saturated acids, such as stearic acid.

(4) *Sabatier's Dehydrogenation Process.* Sabatier and his associates also showed, that at a given temperature, either water, or hydrogen, may be split off from alcohols, depending upon the nature of the catalyst employed. Such finely divided metals as copper, cobalt, nickel, iron, platinum and palladium, together with such anhydrous oxides as the lower oxides of manganese, tin, uranium, molybdenum and vanadium, have been found to function as catalysts in the dehydrogenation process. The dehydrogenation of both primary and secondary alcohols is most readily brought about by the use of reduced copper as a catalyst. On passing an aliphatic alcohol over the latter, at a temperature of 200° to 300°, a yield of fully 50 per cent aldehyde, or ketone, may reasonably be expected.

The chief technical application of this process is to the production of formaldehyde from methyl alcohol. In this process, air is drawn through methyl alcohol, maintained at a temperature suitable for saturation, and the mixture is then passed into a reaction chamber, over copper gauze, as a catalyst. The reaction which occurs may be represented by the equations,

$$2\,CH_3OH + O_2 = 2\,HCHO + 4\,H + O_2 = 2\,HCHO + 2\,H_2O.$$

(5) *Removal of Carbon Monoxide from the Air.* The presence of varying amounts of carbon monoxide in the air, due to the incomplete combustion of solid and liquid fuels, together with its presence in the products of combustion of smokeless powder, renders

the development of adequate means for its elimination of the utmost importance, alike in times of peace and in times of war. A method for its elimination has recently been devised by Lamb, Bray and Frazer.* After much experimentation, it was found that when a mixture of air and carbon monoxide is passed, at ordinary temperatures, over a catalyst consisting of 50 per cent MnO_2, 30 per cent CuO, 15 per cent Co_2O_3, and 5 per cent Ag_2O, the carbon monoxide is completely oxidized to carbon dioxide. This catalytic mixture, called " hopcalite " by its discoverers, has been shown to be capable of acting indefinitely against any concentration of carbon monoxide, provided the air is dry.

(6) *The Welsbach Mantle.* The ignited Welsbach incandescent gas mantle consists of a fragile web of the oxides of thorium and cerium. Pure thoria gives relatively little light, but if progressive amounts of ceria are added, the luminosity gradually increases and attains maximum brightness when 1 per cent of ceria has been added. It is believed, that this increase in luminosity is due to the alternate oxidation and reduction of the ceria, as indicated by the equation,

$$O_2 + 2\ Ce_2O_3 \rightleftarrows 4\ CeO_2.$$

The presence of 1 per cent of ceria in the mixture is sufficient to insure maximum velocity of surface combustion.

The Rôle of Ferments and Enzymes in Catalysis. It is apparent, that catalysis is of great importance in connection with many industrial processes as well as in the field of pure chemistry. The majority of the reactions occurring within living organisms have likewise been found to be accelerated catalytically by unorganized ferments, or enzymes. Thus, before the process of digestion can proceed, starch must be changed into sugar. This transformation is accelerated by an enzyme called *ptyalin* occurring in the saliva, and by other enzymes found in the pancreatic juice. The digestion of albumen is hastened by the enzymes, *pepsin* and *trypsin*. As a rule, each enzyme acts catalytically on just one reaction, or in other words, the catalytic action of enzymes is specific. Enzymes are very sensitive to traces of certain toxic substances such as hydrocyanic acid, iodine, and mercuric chloride.

An interesting series of experiments by Bredig † on the cataly-

* Jour. Ind. Eng. Chem., 12, 213 (1920).

† Zeit. phys. Chem., 31, 258 (1899).

tic action of colloidal metals, established the fact that these substances resemble the enzymes very closely in their behavior. Thus, they are " poisoned " by the same substances which inhibit the activity of the enzymes, and they show the same tendency to recover when the amount of the poison does not exceed a certain limiting value. Because of this close similarity, Bredig called the colloidal metals *inorganic ferments*.

Among the numerous applications of ferments in chemical technology, we shall limit ourselves to the mention of but a single example. The increased demand for acetone and fusel oil, as solvents, has led to the development, by Fernbach, of an interesting fermentation process for the production of these substances. The Fernbach process may be outlined as follows: — Corn, or any similar material rich in carbohydrates, is sterilized at 130°, made into a wort with water, and, after adding a small amount of degraded yeast, the mixture is again sterilized. When cool, an anerobic fermentation process is conducted by means of an appropriate ferment, at a temperature of about 30°. The mass is then distilled, when a yield of from 33 to 50 per cent of acetone and fusel oil, calculated on the basis of the amount of carbohydrate used, is obtained.

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PROBLEMS

1. When a solution of dibromsuccinic acid is heated, the acid decomposes into brom-maleic acid and hydrobromic acid according to the equation,

$$\begin{matrix}\mathrm{CHBr{\cdot}COOH}\\ |\\ \mathrm{CHBr{\cdot}COOH}\end{matrix} = \begin{matrix}\mathrm{CH{\cdot}COOH}\\ \|\\ \mathrm{CBr{\cdot}COOH}\end{matrix} + \mathrm{HBr}.$$

At 50°, the initial titre of a definite volume of the solution was $T_0 = 10.095$ cc. of standard alkali. After t minutes, the titre of the same volume of solution was T_t cc. of standard alkali.

t	0	214	380
T_t	10.09	10.37	10.57

(a) Calculate the velocity-constant of the reaction.

(b) After what time is one-third of the dibromsuccinic acid decomposed? *Ans.* (a) 0.00026; (b) 1559 min.

2. From the following data show that the decomposition of H_2O_2 in aqueous solution is a unimolecular reaction:

Time in minutes	0	10	20
n	22.8	13.8	8.25 cc.

n is the number of cubic centimeters of potassium permanganate required to decompose a definite volume of the hydrogen peroxide solution.

3. In the saponification of ethyl acetate by sodium hydroxide at 10°, y cc. of 0.043 molar hydrochloric acid were required to neutralize 100 cc. of the reaction mixture, t minutes after the commencement of the reaction.

t	0	4.89	10.37	28.18	infinity
y	61.95	50.59	42.40	29.35	14.92

Calculate the velocity-constant, when the concentrations are expressed in mols per liter. *Ans.* Mean value of $k = 2.38$.

4. The velocity-constant of formation of hydriodic acid from its elements is 0.00023; the equilibrium constant at the same temperature is 0.0157. What is the velocity-constant of the reverse reaction?

Ans. 0.0146.

5. Determine the order of the following reaction:

$$6\,FeCl_2 + KClO_3 + 6\,HCl = 6\,FeCl_3 + KCl + 3\,H_2O.$$

When the initial concentration of the reacting substances is 0.1, the changes in concentration at successive times are as follows:

Time (minutes).	Change in Concentration.
5	0 0048
15	0.0122
35	0.0238
60	0 0329
110	0.0452
170	0.0525

6. Calculate the relative rates at which a crystalline solid will dissolve in its own solution, (a) when the solution is 40 per cent saturated, and (b) when it is 90 per cent saturated.

7. The velocity constants in the reaction represented by the equation

$$2\,AsH_3 = 2\,As + 3\,H_2,$$

are $k = 0.00035$ at 256°, and $k = 0.0034$ at 367°. Calculate the value of the velocity constant at 400°.

CHAPTER XV

ELECTRICAL CONDUCTANCE

Historical Introduction. In a book of this character it is impossible to give anything like a complete historical sketch of electrochemistry. Before entering upon an outline of this interesting division of theoretical chemistry, however, it is desirable to consider very briefly a few of the theories which have played a prominent part in the development of our modern views concerning electrochemical phenomena.

While the early observations of Beccaria and others pointed to the probability of the existence of some relation between chemical and electrical phenomena, it was not until the beginning of the nineteenth century that the science of electrochemistry had its birth. The epoch-making discovery, by Volta, of a means of obtaining electrical energy from chemical energy, gave the initial impulse to all the brilliant discoveries and investigations upon which the modern science of electrochemistry is based. The apparatus devised by Volta, known as the *voltaic pile*, consisted of disks of zinc and silver placed alternately over one another, the silver disk of one pair being separated from the zinc disk of the next, by a piece of blotting paper moistened with brine. Such a pile, if composed of a sufficient number of pairs of disks, will produce electricity enough to give a shock, if the top and bottom disks, or wires connected with them, be touched with the moist fingers. This discovery placed in the hands of the investigator a source of electricity by means of which experiments could be performed which had hitherto been impossible.

Shortly after the discovery of the voltaic pile, Nicholson and Carlisle* effected the decomposition of water, and Davy† isolated the alkali metals. As a result of these experiments, Davy was led to formulate his electrochemical theory. According to this theory,

* Nich. Jour., 4, 179 (1800).

† Ibid., 4, 275, 326 (1800); Gilb. Ann., 7, 114 (1801).

the atoms of different substances acquire opposite electrical charges by contact, and thus mutually attract each other. If the differences between the charges are small, the attraction will be insufficient to cause the atoms to leave their former positions; if it is great, a rearrangement of the atoms will occur, and a chemical compound will be formed. In terms of this theory, electrolysis consists in a neutralization of the charges upon the atoms.

The theory of Davy was soon superseded by that of Berzelius.* According to the latter theory, every atom is charged with both kinds of electricity, which exist upon the atoms in a polar arrangement, the electrical behavior of the atom being determined by the kind of electricity which is in excess. Chemical attraction is thus ascribed to the electrical attraction of oppositely-charged atoms. Since each atom is endowed with both positive and negative electrification, one charge being in excess, it follows that the compound formed by the union of two or more atoms will be positively or negatively charged, according to whichever charge remains unneutralized after the atoms have combined. Two compounds, the one charged positively and the other negatively, may thus in turn combine, a more complex compound being formed. Shortly after Berzelius formulated his theory, it became the subject of much discussion and was severely criticized. Thus, it was pointed out, that if chemical combination results from the neutralization of oppositely-charged atoms, then as soon as the charges have become equalized, there will no longer exist any attractive force, and the compound will again decompose. This objection was easily overcome by assuming, that as soon as the union between the atoms is broken, they will again acquire their original charges, and in consequence, will recombine. In other words, a chemical compound is to be regarded as existing in a state of unstable equilibrium.

Another, and apparently insurmountable objection to the theory, resulted from the exceptions presented by acetic acid and some of its substitution products. According to the theory of Berzelius, chemical combination is entirely dependent upon the nature of the electrical charges residing on the atoms. From this statement it follows, that the properties of a chemical compound must be a function of the electrical charges upon the atoms of its constituents. It was shown, that when the three hydrogen atoms

* Gilb. Ann., 27, 270 (1807).

of the methyl group in acetic acid are successively replaced by chlorine, the chemical properties of the original substance are not materially altered. According to Berzelius, the three hydrogen atoms are positively charged, while the three chlorine atoms are negatively charged. That three negative charges could be substituted for three positive charges, in acetic acid, without producing a more marked change in its properties, could not be satisfactorily explained. This criticism was for a long time considered to be an insuperable barrier to the acceptance of the theory. Shortly before the close of the nineteenth century, J. J. Thomson* showed that this objection has little or no weight. When hydrogen gas was electrolyzed in a vacuum-tube, and the spectra at the two electrodes were compared, Thomson found them to differ widely. From this he concluded that the molecule of hydrogen gas is, in all probability, made up of positively- and negatively-charged parts, or ions. He then extended his experiments to the vapors of certain organic compounds. In discussing these experiments he says: — "In many organic compounds, atoms of an electropositive element, hydrogen, are replaced by atoms of an electronegative element, chlorine, without altering the type of the compound. Thus, for example, we can replace the four hydrogen atoms in CH_4 by chlorine atoms, getting, successively, the compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. It seemed of interest to investigate what was the nature of the charge of electricity on the chlorine atoms in these compounds. The point is of some historical interest, as the possibility of substituting an electronegative element in a compound for an electropositive one was one of the chief objections against the electrochemical theory of Berzelius."

"When the vapor of chloroform was placed in the tube, it was found that both the hydrogen and chlorine lines were bright on the negative side of the plate, while they were absent from the positive side, and that any increase in brightness of the hydrogen lines was accompanied by an increase in the brightness of those due to chlorine. The appearance of the hydrogen and chlorine spectra on the same side of the plate was also observed in methylene chloride and in ethylene chloride. Even when all the hydrogen in methane was replaced by chlorine, as in carbon tetrachloride, the chlorine spectra still clung to the negative side of

* Nature, 52, 451 (1895).

the plate. The same point was tested with silicon tetrachloride and the chlorine spectrum was brightest on the negative side of the plate. From these experiments it would appear, that the chlorine atoms in the chlorine derivatives of methane are charged with electricity of the same sign as the hydrogen atoms they displace."

Electrical Units. In 1827, Dr. G. S. Ohm enunciated his well-known law of electrical conductance, viz.: — *The strength of the electric current flowing in a conductor is directly proportional to the difference of potential between the ends of the conductor, and inversely proportional to its resistance.* If I represents the strength of the current, E the difference of potential, and R the resistance, then Ohm's law may be formulated as follows:

$$I = \frac{E}{R}. \tag{1}$$

The unit of resistance is the *ohm*, that of difference of potential, or electromotive force, the *volt*, and that of current, the *ampere*. The ohm is defined as the resistance offered to an unvarying current by a column of mercury at 0° C., 14.4521 grams in mass, 106.300 cm. in length, and of constant cross-section. The ampere is defined as the current which will cause the deposition of 0.001118 gram of silver from a solution of silver nitrate in 1 second. The volt may be defined as the electromotive force necessary to drive a current of 1 ampere through a resistance of 1 ohm. The unit quantity of electricity is the *coulomb*. This amount of electricity passes when a current of a strength of one ampere flows for one second. One gram-equivalent of any ion carries 96,500 coulombs. This quantity of electricity is known as the *faraday* and is commonly represented by the letter F.

As has already been pointed out, any form of energy may be considered as the product of two factors, a capacity factor and an intensity factor. The capacity factor of electrical energy is the coulomb, while the intensity factor is the volt, i.e.,

$$\text{electrical energy} = \text{coulombs} \times \text{volts}.$$

The unit of electrical energy, therefore, is the *volt-coulomb*, or *joule*, commonly called the *watt-second*. One watt-second is the electrical work done by a current of 1 ampere flowing under an electromotive force of 1 volt for 1 second, and is equivalent to 1×10^7 ergs.

Experiment has shown that 0.4272 kg.-m. of mechanical energy is equivalent to 1 calorie and that 4.182 joules of electrical energy are also equivalent to 1 calorie. It follows, therefore, that

$$1 \text{ joule} = \frac{1}{4.182} = 0.2387 \text{ calorie} = 1 \times 10^7 \text{ ergs.}$$

Faraday's Law. If two platinum plates or electrodes, one connected to the positive, and the other to the negative terminal of a battery, are immersed in a solution of sodium chloride, it will be found that hydrogen is immediately evolved at the negative electrode and oxygen at the positive electrode. If the salt solution is previously colored with a few drops of a solution of litmus, it will be observed that the portion of the solution in the neighborhood of the positive electrode will turn red, indicating the formation of an acid, while that in the neighborhood of the negative electrode will turn blue, showing the formation of a base. The same changes will take place whether the electrodes are placed near together or far apart, and furthermore, the evolution of gas and the change in color at the electrodes commences as soon as the circuit is closed. The study of these phenomena led Faraday * to the conclusion, that when an electric current traverses a solution, there occurs an actual transfer of matter, one portion travelling with the current, and the other portion moving in the opposite direction. Faraday termed these carriers of the current, *ions*. He also called the electrode connected to the positive terminal of the battery, the *anode*, and the electrode connected to the negative terminal, the *cathode*. The ions which move toward the anode he called *anions*, while those which migrate toward the cathode he called *cations*. The whole process he termed *electrolysis*.

The question of the relationship between the amount of electrolysis and the quantity of electricity passing through a solution, was first investigated by Faraday. As a result of his experiments he enunciated the following law, which is commonly known as the law of Faraday:

(1) *For the same electrolyte, the amount of electrolysis is proportional to the quantity of electricity which passes.*

(2) *The amounts of substances liberated at the electrodes, when the same quantity of electricity passes through solutions of different elec-*

* Experimental Researches (1834).

trolytes, are proportional to their chemical equivalents. The *chemical equivalent* of any ion is defined as the ratio of the atomic weight of the ion to its valence. If the same quantity of electricity is passed through solutions of hydrochloric acid, silver nitrate, cuprous chloride, cupric chloride, and auric chloride, the relative amounts of the respective cations liberated will be as follows: — $H^{\cdot} = 1$, $Ag^{\cdot} = 108$, $Cu^{\cdot} = 63.4$, $Cu^{\cdot\cdot} = 63.4/2$ and $Au^{\cdot\cdot\cdot} = 197/3$.

The *electrochemical equivalent* of an element or group of elements is the weight in grams which is liberated by the passage of one coulomb of electricity. The electrochemical equivalents are, according to Faraday's law, proportional to the chemical equivalents.

As has been pointed out, the quantity of electricity necessary to liberate one chemical equivalent in grams is 96,500 coulombs. Since 96,500 coulombs of electricity liberate one gram equivalent of hydrogen, it follows that $1.008 \div 96{,}500 = 0.0000104463$ gram of hydrogen will be liberated by 1 coulomb. The same quantity of electricity will liberate $35.45 \times 0.0000104463 = 0.00036749$ gram of chlorine, and $108 \times 0.0000104463 = 0.001118$ gram of silver. Or, in general, since one coulomb of electricity liberates 0.0000104463 gram of hydrogen, it will cause the liberation of $0.0000104463\ w$ grams of any other element whose equivalent weight is w.

A large amount of experimental work has been done on the electrolysis of solutions of silver nitrate with a view to the precise determination of the electrochemical equivalent of silver and the definition of the ampere.* The value of the faraday has recently been determined by Vinal and Bates† with an experimental error not exceeding 0.01 per cent. In this investigation, solutions of silver nitrate and potassium iodide were electrolyzed in the same circuit, and the weights of silver and iodine liberated were determined. These experiments furnish an admirable confirmation of the laws of Faraday, as may be seen by the following table giving the summary of the results obtained by Vinal and Bates.

* Bull. Bureau of Standards, 1, 1 (1904); 9, 494 (1912); 10, 425 (1914); 11, 220, 555 (1914); Richards, Proc. Am. Acad., 37, 415 (1902); 44, 91 (1908); Jour. Am. Chem. Soc., 37, 692 (1915).

† Bull. Bureau of Standards, 10, 425 (1914).

DETERMINATION OF THE FARADAY

Mean Silver Deposit	Mean Iodine Deposit	Calculated Coulombs		Ratio Silver: Iodine	Electrochemical Equivalent of Iodine	Value of the Faraday (I = 126.92)
		From Ag. Voltameter	From Cell and Res.			
mg	mg					
4105.82	4829.59	3672.47	.....	0.85013_8	1.31508	96 511
4104.69	4828.62	3671.45	3671.53	07_5	518	504
4099.03	4822.24	3666.39	3666.55	02_6	526	498
4397.11	5172.73	3933.01	.....	05_6	521	502
4105.23	4828.51	3671.94	3671.84	20_5	498	518
4123.10	4849.42	3687.92	.....	22_6	495	521
4104.75	4828.60	3671.51	3671.61	09_1	515	506
4184.24	4921.30	3742.61	.....	23_3	494	521
4100.27	4822.47	3667.50	3667.65	24_2	492	523
4105.16	4828.44	3671.88	3671.82	20_4	498	519
				0.85016	1.31505	96 514
Weighted mean (all observations)				0.85017	1.31502	96 515

The law of Faraday is among the very few generalizations to which there do not appear to be any exceptions. This law has been found to hold with the same exactness in both dilute and concentrated solutions, at low and high temperatures,* at low and high pressures and also in all solvents.†

Coulometers. The quantity of electricity passing through an electric circuit is measured by means of an electrolytic cell, which is so arranged as to allow the amount of chemical change occurring at an electrode surface to be accurately determined. Such a cell is known as a *coulometer*. There are three general types of coulometers in use, namely, (1) *weight coulometers*, in which the quantity of electricity is measured by the gain in weight of the cathode, due to the deposition of metal from the electrolyte; (2) *volume coulometers*, in which the volume of electrolytic gas liberated by the passage of the current is measured; and (3) *titration coulometers*, in which the change in concentration of the electrolyte at one of the electrodes is determined by titration with a standard solution. Of these three types, the most accurate is the silver coulometer in which silver is deposited from a solution of silver nitrate upon a

* Richards and Stull, Proc. Am. Acad., 38, 409 (1902).

† Kahlenberg, Jour. Phys. Chem., 4, 349 (1900).

weighed platinum dish as a cathode.* For industrial purposes the copper coulometer is usually employed. This is also a weight coulometer, and consists of two sheets of pure copper as an anode between which is placed a single weighed sheet of thin copper as a cathode, while a solution of copper sulphate serves as the electrolyte.

The Existence of Free Ions. When an electrolyte is decomposed by the electric current, the products of decomposition appear at the electrodes. The fact that the liberation of the products of decomposition is independent of the distance between the electrodes caused considerable difficulty in the early history of electrochemistry. It was evident that the two products could hardly be derived from the same molecule, but must come from two different molecules. Several theories were advanced to account for the experimental results. Thus, in the electrolysis of water it was suggested that the two gases, hydrogen and oxygen, were not derived from the water, but that electricity itself possessed an acid character. Grotthuss† was the first to propose a rational hypothesis as to the mechanism of electrolysis. He assumed, that when the electrodes in an electrolytic cell are connected with a source of electricity, the molecules of the electrolyte arrange themselves in straight lines between the electrodes, the positive poles being directed toward the negative electrode and the negative poles toward the positive electrode. When electrolysis begins, the cation of the molecule nearest the cathode is liberated at the cathode, and the anion of the molecule nearest the anode is liberated at the anode. The anion which is left free near the cathode then combines with the cation of the next adjoining molecule, while the anion thus left uncombined, unites with the cation of its nearest neighbor. A similar exchange of partners is assumed to take place throughout the entire molecular chain. Under the directive influence of the two electrodes, the newly-grouped molecules then rotate, so that all of the positive poles face the negative electrode and all of the negative poles face the positive electrode.

An inherent defect in this theory was discovered by Grove.‡ From his experiments with the oxy-hydrogen cell, which derives

* See Bull. Bureau of Standards, 1, 3 (1904).

† Ann., de Chim. [1], 58, 54 (1806).

‡ Phil. Mag., 27, 348 (1845).

its energy from the union of hydrogen and oxygen, he concluded that a decomposition of the molecules of water is not essential for the evolution of these two gases, but that the molecules must be present initially in a state of partial decomposition.

This suggestion was followed up by Clausius.* He argued that if an expenditure of energy is necessary to decompose the molecules, electrolysis should be impossible at very low voltages. Experiment showed, that when silver nitrate is electrolyzed between silver electrodes, decomposition takes place at voltages which are much below the voltage corresponding to the energy of formation of silver nitrate. In other words, it requires very little energy to decompose a salt which is formed with the evolution of a large amount of energy, a result which is in contradiction to the principle of the conservation of energy. Clausius was thus forced to conclude, "that the supposition that the constituents of the molecule of an electrolyte are firmly united and exist in a fixed and orderly arrangement is wholly erroneous."

As a result of his investigation of the synthesis of ethyl ether from alcohol and sulphuric acid, Williamson† concluded "that in an aggregate of the molecules of every compound, a constant interchange between the elements contained in them is taking place." In the same paper he writes, "each atom of hydrogen does not remain quietly attached all the time to the same atom of chlorine, but they are continually exchanging places with one another." This view was accepted by Clausius, although he had no means of determining the extent to which the electrolyte was broken down, or dissociated into free ions.

In 1887, Arrhenius ‡ developed the views of Clausius by showing how the degree of dissociation of the molecules of an electrolyte can be deduced from measurements of the electrical conductance of its solutions, as well as from measurements of osmotic pressure and freezing-point lowering. The important generalization summarizing these conceptions is none other than the theory of electrolytic dissociation, to which reference has already been made in an earlier chapter (see page 262).

The Migration of the Ions. Since the passage of a current of electricity through a solution of an electrolyte, causes the dis-

* Pogg. Ann., 101, 338 (1857).
† Lieb. Ann., 77, 37 (1851).
‡ Zeit. phys. Chem., 1, 631 (1887).

charge of equivalent amounts of positive and negative ions at the electrodes, it might be inferred that all of the ions move with the same speed. That this inference is incorrect, was first shown by Hittorf,* as the result of his observations on the changes in concentration of the solution in the neighborhood of the electrodes during electrolysis. He showed that different ions migrate with different speeds, and that the faster moving ions carry a greater proportion of the current than the slower moving ions. The effect of unequal ionic velocities on the concentrations of the solutions around the electrodes is clearly shown by the accompanying diagram, (Fig. 128), due to Ostwald. The anode and

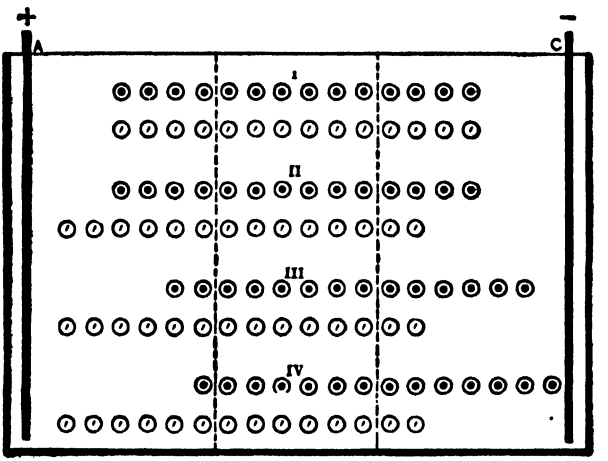

Fig. 128

cathode in an electrolytic cell are represented by the vertical lines, *A* and *C*, respectively. The cell is divided into three compartments by means of porous diaphragms, represented by the vertical dotted lines. The cations are represented by dots (˙), and the anions by dashes (′). Before the current passes through the cell, the concentration of the solution is uniform throughout, the conditions being represented by I. Now let us imagine that only the anions move when the circuit is closed. The conditions, when the chain of anions has moved two steps toward the anode, are shown in II. Each ion which has been deprived of a partner is supposed to be discharged. It will be observed, that although

* Pogg. Ann., 89, 177; 98, 1; 103, 1; 106, 337, 513 (1853–1859).

the cations have not migrated toward the cathode, yet an equal number of positive and negative ions are discharged, and furthermore that while the concentration in the anode compartment has not changed, the concentration in the cathode compartment has diminished to one-half its original value. Let us now suppose that both anions and cations move with the same speed, and as before, let each chain of ions move two steps toward their respective electrodes, as indicated in III. It will be seen, that four positive and four negative ions have been discharged, and that the concentration of the electrolyte in the anode and cathode compartments has diminished to the same extent. Finally, let us assume that the ratio of the speed of the cations to that of the anions is as 3 : 2. When the cations have moved three steps toward the cathode and the anions have moved two steps toward the anode, the conditions will be as shown in IV. It is evident that five positive and five negative ions have been discharged, and that the concentration in the cathode compartment has diminished by two molecules, while the concentration in the anode compartment has diminished by three molecules. It will be observed, that the change in concentration in either of the electrode compartments is proportional to the speed of the ion leaving it. Thus, in II, the concentration in the cathode compartment diminishes, while that in the anode compartment remains unchanged, since only the anion moves. In like manner, the change in concentration about the electrodes in III corresponds with the fact that both ions migrate at the same rate. In IV, the ratio of the change in concentration in the cathode compartment to that in the anode compartment is as 2 : 3. It will be apparent from these examples, that the relation between the speeds of the anions and the corresponding changes in concentration at the electrodes may be expressed by the following proportion:

$$\frac{\text{Change in concentration at anode due to migration}}{\text{Change in concentration at cathode due to migration}} = \frac{\text{speed of cation}}{\text{speed of anion}} = \frac{u}{v}$$

If the relative speed of the cations is represented by u, and that of the anions by v, then the total quantity of electricity transported will be proportional to $u + v$: of this total, the fractions carried by the anion and cation, respectively, will be $n_a = \frac{v}{u+v}$,

and $1 - n_a = n_c = \frac{u}{u+v}$. The values of these ratios, n and $1 - n$, are called the Hittorf *transference numbers* of the anion and cation respectively. It is apparent from the diagram, that if the electrolysis is not carried too far, the concentration of the solution in the intermediate compartment will undergo no change. In order to determine transference numbers, therefore, it is simply necessary to remove portions of the solutions in the immediate vicinity of the two electrodes and determine the change in the concentration of the electrolyte resulting from the passage of a known amount of electricity. The success of the experiment depends upon keeping the concentration of the intermediate compartment unaltered.

Experimental Determination of Transference Numbers. Various forms of apparatus have been constructed for the determination of transference numbers, among which that devised by the author,* and shown in Fig. 129, has proven very satisfactory. It consists of two vertical tubes of wide bore, connected by a horizontal tube of the same diameter. The electrodes, of suitable metal in the form of wire are wound spirally around the glass connecting tubes. The wire spirals are soldered to short pieces of platinum wire which serve to establish electrical connection with mercury in the connecting tubes, the junction of the two wires being covered with a drop of fusion glass. The tubes by which electrical connection is established are held in place by means of rubber stoppers having a groove cut on one side to allow for possible expansion of the contents of the cell. The outlet tubes of the two arms are provided with rubber caps to protect them from contamination with the water of the thermostat. In carrying out a determination of a transference number, the cell is filled with the solution of the electrolyte to be studied and included in a circuit containing a variable resistance, a silver coulometer, a milli-ammeter and a voltmeter. The current is then allowed to pass through the appa-

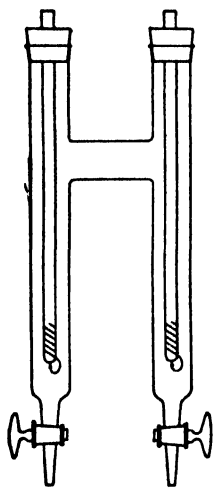

Fig. 129

* Jour. Am. Chem. Soc., 36, 1640 (1914).

ratus until a sufficient change in concentration has taken place in the anode and cathode compartments, when the circuit is broken and the amount of this change is determined analytically. The portions of the solutions in the two halves of the apparatus are drawn out into separate beakers, and the concentration of each is determined. Knowing the initial concentration of the solution and the final concentrations at the two electrodes, together with the total quantity of electricity which has passed through the apparatus during the experiment, we have all of the data necessary for the calculation of the transference numbers of the two ions.

The following example will serve to make the method of calculation clear: — In an experiment to determine the transference numbers of the ions of silver nitrate, a solution containing 0.00739 gram of that salt per gram of water was prepared. The solution was introduced into the migration apparatus and, after inserting silver electrodes, a small current was passed through the apparatus for two hours. A silver coulometer was included in the circuit, and 0.0780 gram of silver was deposited by the current. This mass of silver is equivalent to 0.000723 gram-equivalent. After the circuit was broken, the anode solution was rinsed out and its concentration determined analytically. It was found to contain 0.2361 gram of silver nitrate to 23.14 grams of water. This amount of solution contained originally $23.14 \times 0.00739 = 0.1710$ gram of silver nitrate. Thus, the amount of silver nitrate in the anode compartment had increased by $0.2361 - 0.1710 = 0.0651$ gram of silver nitrate, or 0.000383 gram-equivalent of silver. Obviously, the increase in the concentration of the nitrate ion must have been the same. The amount of silver dissolved from the anode must have been equal to that deposited in the coulometer, or since 0.000723 gram-equivalent of silver was deposited, and the actual increase found was 0.000383 gram-equivalent, the difference, $0.000723 - 0.000383 = 0.000340$ gram-equivalent, is the amount of silver which migrated away from the anode. At the same time, 0.000383 gram-equivalent of nitrate ions migrated into the anode compartment. The ratio of the speed of migration of the silver ions to that of the nitrate ions is as 0.000340 : 0.000383. But 0.000723 gram-equivalent of silver ions measures the total quantity of electricity transported, therefore the transference numbers of the two ions will be as follows:

$$\text{Transference number of } Ag^{\cdot} = n_c = \frac{0.000340}{0.000723} = 0.470,$$

$$\text{Transference number of } NO_3' = n_a = \frac{0.000383}{0.000723} = 0.530.$$

These numbers can be checked by a similar calculation based on the change in concentration in the cathode compartment.

The following table gives the transference numbers of the cations of several typical electrolytes, at different concentrations and different temperatures. The transference number of the corresponding anions can be found by subtracting the transference numbers of the cations from unity.

TRANSFERENCE NUMBERS OF CATIONS*

Electrolyte	Temp.	Concentration					
		0.005	0.01	0.02	0.05	0.10	0.20
NaCl	0°	0.387	0.387	0.387	0.386	0.385	....
	18	0.396	0.396	0.396	0.395	0.393	....
	30	0.404	0.404	0.404	0.404	0.403	....
KCl	0	0.493	0.493	0.493	0.493	0.492	0.491
	18	0.496	0.496	0.496	0.496	0.495	0.494
	30	0.498	0.498	0.498	0.498	0.497	0.496
LiCl	18	....	0.332	0.328	0.320	0.313	0.304
NH_4Cl	18	....	0.492	0.492	0.492	....	....
$AgNO_3$	18	....	0.471	0.471	0.471	0.471	....
	30	0.481	0.481	0.481	0.481	0.481	0.481
HCl	0	0.847	0.846	0.844	0.839	0.834	....
	18	0.832	0.832	0.833	0.833	0.834	0.837
HNO_3	20	0.839	0.840	0.841	0.844	....	....
$BaCl_2$	0	0.439	0.437	0.432	....	....	....
	25	....	....	....	0.438	0.427	0.415
$CaCl_2$	20	0.440	0.432	0.424	0.413	0.404	0.395
H_2SO_4	20	....	....	0.822	0.822	0.822	0.820
$MgSO_4$	18	0.388	0.385	0.381	0.373	....	....
$CuSO_4$	18	....	....	0.375	0.375	0.373	0.361

* Noyes and Falk, Jour. Am. Chem. Soc., 33, 1454 (1911).

It is apparent from the table that the transference numbers are not entirely independent of the concentration, and also that they vary slightly with the temperature. In fact, with rising temperature, the transference numbers of all ions tend to become equal, the limiting value beng 0.5.

Transference Numbers and Ionic Hydration. In the method just outlined for the determination of transference numbers, it was assumed that the solvent remains stationary during the passage of the current, and that the change in concentration, which occurs in the vicinity of the electrode, is due to the difference in the relative speeds with which the ions move through the solution.

That this assumption is not correct has been proven by Washburn and Millard,* who have demonstrated experimentally that the ions are hydrated and carry a portion of the solvent with them from one electrode to the other. While the amount of solvent thus transferred, in dilute solutions, is exceedingly small, it becomes sufficiently large, in concentrated solutions, to affect the values of the transference numbers. If an inert substance, such as sucrose, be added to the solution in a transference experiment, it will remain stationary during the passage of the current, and may be used as a reference substance to determine the amount of solvent which has been transported by the ions. In this manner, Washburn and Millard determined the so-called "true" transference numbers given in the accompanying table.

TRUE TRANSFERENCE NUMBERS AT 25°

Electrolyte Concentration 1.3 Molar	n_w/n_c'	n_w	n_c'	n_∞	n_c
HCl.....	0.28	0.24	0.844	0.833	0.820
CsCl.....	0.67	0.33	0.491	0.491	0.485
KCl.....	0.3	0.60	0.495	0.495	0.482
NaCl.....	2.0	0.76	0.383	0.396	0.366
LiCl.....	4.7	1.5	0.304	0.330	0.278

n_w = number of mols of water transferred from anode to cathode per faraday,
n_c' = true transference number of cation,
n_∞ = transference number at infinite dilution,
n_c = Hittorf transference number.

In dilute solutions, the difference between Hittorf and true transference numbers is so small as to be negligible. If n_w denotes the number of mols of water transferred from the anode to the cathode per faraday of electricity, and N_s/N_w is the ratio of the

* Jour. Am. Chem. Soc., 37, 694 (1915).

number of mols of the solute to the number of mols of water in the original solution, the relation between the Hittorf transference number of the anion, n_a, and the true transference number of the anion, n_a', will be given by the equation,

$$n_a' = n_a - n_w \frac{N_s}{N_w}. \tag{2}$$

Specific, Molar and Equivalent Conductance. As is well known, the resistance of a metallic conductor is directly proportional to its length and inversely proportional to its area of cross-section. Similarly, the resistance of an electrolyte is proportional to the length, and inversely proportional to the cross-section of the column of solution between the two electrodes. The *specific resistance* of an electrolyte may be defined as the resistance in ohms of a column of solution one centimeter long and one square centimeter in cross-section. *Specific conductance* is the reciprocal of specific resistance. Since the conductance of a solution is almost wholly dependent upon the amount of solute present, it is more convenient to express conductance in terms of the molar, or equivalent concentration. The *molar conductance* μ, is the conductance, in reciprocal ohms, of a solution containing one mol of solute when placed between electrodes which are exactly one centimeter apart. The *equivalent conductance* Λ, is the conductance, in reciprocal ohms, of a solution containing one gram-equivalent of solute when placed between electrodes which are one centimeter apart. If L denotes the specific conductance of a solution, and V_m the volume in cubic centimeters which contains one mol of solute, then

$$\mu = LV_m, \tag{3}$$

and in like manner,

$$\Lambda = LV_e, \tag{4}$$

where V_e is the volume of solution in cubic centimeters which contains one gram-equivalent of solute. If C denotes the concentration of a solution of an electrolyte in gram-equivalents per liter, equation (4) becomes,

$$\Lambda = \frac{1000\,L}{C}. \tag{5}$$

The following table gives the specific and equivalent conductance of solutions of sodium chloride at 18° C.:

CONDUCTANCE OF SOLUTIONS OF SODIUM CHLORIDE

Concentration	Dilution	Sp. Cond.	Molar Cond.
1	1,000	0.0744	74.4
0.1	10.000	0.00925	92.5
0.01	100,000	0.001028	102.8
0.001	1,000,000	0.0001078	107.8
0.0001	10,000,000	0.00001097	109.7

It will be observed that the equivalent conductance increases with the dilution up to a certain point, beyond which it remains nearly constant. That the equivalent conductance should change but little will become apparent from the following considerations. Imagine a rectangular cell of indefinite height and having a cross-sectional area of one square centimeter, and further assume that two opposite walls can function as electrodes. Let 1000 cc. of a solution, containing one equivalent of solute, be introduced into the cell, and let its conductance be determined. Now let the solution be diluted to 2000 cc., and the conductance of the diluted solution be measured. While the specific conductance of the diluted solution is reduced to one-half of its original value, yet, since the solution stands at twice the original height in the cell, the electrode surface in contact with the solution is doubled, and the total conductance due to one mol of solute remains unchanged. This, of course, is only the case with completely ionized solutes.

Determination of Electrical Conductance. The determination of the electrical conductance of a solution resolves itself into the determination of its resistance, by a simple modification of the familiar Wheatstone-bridge method. The arrangement of the apparatus for this method, devised by Kohlrausch,* is represented diagrammatically in Fig. 130, where *ab* is the bridge wire, *B* is a resistance box, and *C* is a cell containing the solution whose resistance is to be measured. The points *d* and *c* are connected to a small induction coil, *I*, which gives an alternating current. This is necessary in order to prevent polarization which would occur if a direct current were used. The use of the alternating current necessitates the substitution of a telephone, *T*, for a galvanometer, usually employed in measuring resistance. The

* Wied. Ann., 6, 145 (1879); 11, 653 (1880); 26, 161 (1885).

positions of the induction coil and telephone are sometimes interchanged, but the arrangement shown in the diagram is to be preferred, since it insures a high electromotive force where the sliding contact, *c*, touches the wire, this being the most uncertain connection in the entire arrangement. A small accumulator, *A*, serves to operate the induction coil. Where a higher degree of accuracy is required it is necessary to include a variable air condenser in parallel with the resistance box, *B*, in order to balance the capacity of the conductance cell, *C*.

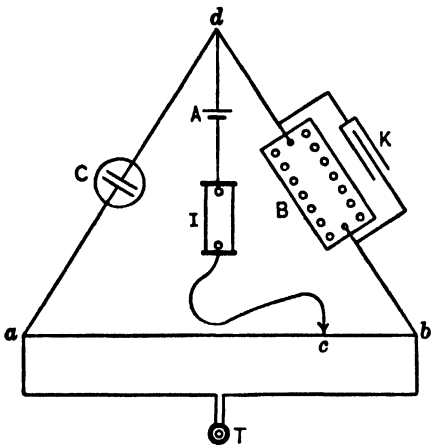

Fig. 130

In making a measurement, the coil is connected with the accumulator, and the vibrator is so adjusted that a high mosquito-like tone is emitted; then the sliding contact, *c*, is moved along the wire, *ab*, until the sound in the telephone reaches a minimum, when the position of the point of contact is read on a millimeter scale placed below the bridge-wire. According to the principle of the Wheatstone bridge, it follows, that

$$\frac{C}{B} = \frac{ac}{bc}.$$

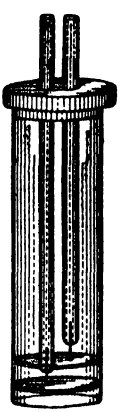
Fig. 131

Since the resistance, *B*, and the lengths, *bc* and *ac*, are known, the resistance, *C*, can be calculated. Various types of conductance cells are in use, depending upon whether the solution has a high, or a low resistance. The form shown in Fig. 131 is widely used. The two electrodes are made of platinum foil, connection with the mercury being established by means of two pieces of stout platinum wire sealed through the ends of the tubes, *tt*. These tubes are fastened into a tight-fitting vulcanite cover so that the electrodes may be removed, rinsed and dried, without altering their relative positions.

It has been pointed out by Washburn* that the area of the cross-section between the electrodes in a properly designed conductance cell should not be less than a certain minimum value which is completely fixed and determined by the audibility current of the telephone, the time required to make the bridge setting, the lowest specific conductance which it is desired to include within the range of the cell, and the percentage accuracy demanded in the measurements. In other words, the conductance cells should be designed to fit the telephone receiver to be used with them. Three types of conductance cell designed by Washburn are shown in Fig. 132: *A* is adapted for specific conductances down as low as 1×10^{-7} reciprocal ohms, *B* for conductances ranging from 1×10^{-6} to 1×10^{-3} reciprocal ohms and *C* for conductances ranging from 1×10^{-4} to 1×10^{-1} reciprocal ohms.

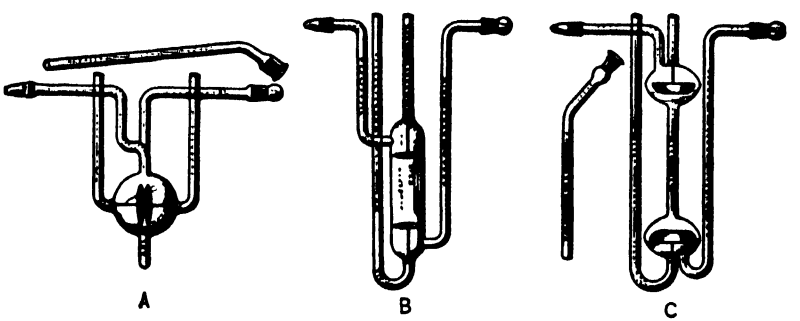

Fig. 132

Before a conductance cell is used, the electrodes must be coated, electrolytically, with platinum black. It is not necessary to know the area of the electrodes, or the distance between them, since it is possible to determine a factor, termed the *resistance capacity*, by means of which the results obtained with the cell can be transformed into reciprocal ohms. To this end, the specific conductances of a number of standard solutions have been carefully determined by Kohlrausch; thus, for a 0.02 molar solution of potassium chloride he found the following values:

$$L_{18^\circ} = 0.002397 \quad \text{and} \quad L_{25^\circ} = 0.002768,$$

or

$$\Lambda_{18^\circ} = 119.85 \quad \text{and} \quad \Lambda_{25^\circ} = 138.4.$$

* Jour. Am. Chem. Soc., 38, 2431 (1916).

Let the resistance of the cell, when filled with 0.02 molar potassium chloride, be C, then, according to the principle of the Wheatstone bridge, we have

$$C = B \cdot \frac{ac}{bc},$$

or, denoting the conductance of the solution by S, we obtain,

$$S = \frac{1}{C} = \frac{ac}{B \cdot bc}.$$

Since the specific conductance, L, must be proportional to the observed conductance, we have

$$L = KS = K\frac{ac}{B \cdot bc},$$

where K is the resistance capacity of the cell. If the measurement is made at 18° C.,

$$K = \frac{0.002397\ B \cdot ac}{bc}.$$

Having determined the resistance capacity of the cell, we may proceed to determine the conductance of any solution. For example, suppose that when the resistance in the box is B', the point of balance on the bridge-wire is at c', then the specific conductance of the solution will be

$$L = K\frac{ac'}{B'bc'}.$$

If L is divided by the concentration in gram-equivalents per liter of the solution, and multiplied by 1000, the equivalent conductance, Λ at that concentration is obtained, or,

$$\Lambda = \frac{1000\ L}{C}.$$

The method just described for the measurement of electrical conductance has recently been modified by Hall and Adams,* who have introduced into the circuit a thermionic amplifier. The advantage of this modification is that the current through

* Hall and Adams, Jour. Am. Chem. Soc., 41, 1515 (1919).

the telephone can be increased almost indefinitely without changing the current flowing through the remainder of the bridge circuit, thus increasing the precision with which the position of balance on the slide-wire of the bridge can be determined.

Relative Conductances of Different Substances. The study of the electrical conductance of various solutes in aqueous solution, reveals the fact that electrolytes differ greatly in their conducting power. They may be roughly divided into two classes: — those with high conducting power, such as strong acids, strong bases, and salts; and those with low conducting power, such as ammonia, and most of the organic acids and bases. The following table gives the equivalent conductances of several typical electrolytes, from normal down to so-called "zero" concentration. In every case it will be observed, that the equivalent conductance increases with the dilution of the solution until a limiting value, Λ_0, is reached. It is important to bear in mind, that although Λ_0 is frequently referred to as the conductance at infinite dilution, it is not identical with the conductance of the pure solvent.

In the case of so-called "strong electrolytes," the value of the limiting conductance, Λ_0, is obtained by extrapolating the values of the conductance at finite concentrations. Although the accuracy of extrapolated data is always more or less uncertain, the error in the extrapolated values of Λ_0, for strong electrolytes, is known to be less than one per cent, in the majority of cases. To minimize the error in extrapolation, Noyes and Falk* plotted the reciprocal of the equivalent conductance, $1/\Lambda$, against $(C\Lambda)^m$ and then, by trial, determined the value of m which would give a straight line. On extending this line until it cuts the axis at a point corresponding to $(C\Lambda)^m = 0$, the limiting value of $1/\Lambda$ was found, and from this the value of the limiting conductance, Λ_0, could easily be calculated. The value of m was found to be approximately 0.5.

The limiting conductance of weak electrolytes cannot be determined by the method just outlined, owing to the fact that, at concentrations below 0.0001 molar, it is very difficult to make satisfactory measurements of conductance, and consequently the method of extrapolation cannot be employed. In order to determine the value of Λ_0, for weak electrolytes, it is necessary to know

* Jour. Am. Chem. Soc., 34, 454 (1912).

the values of the conductance of the individual ions, as determined by the law of Kohlrausch.

EQUIVALENT CONDUCTANCES OF TYPICAL ELECTROLYTES*
Temp. 18°

Normal Conc.	NaCl	KCl	HCl	$NaNO_3$	KNO_3	$AgNO_3$	HNO_3
0.0000	108.9	130.0	380.0	105.2	126.3	115.8	376.5
0.0001	108.0	129.0	378.1	104.5	125.4	115.0	.....
0.0005	107.1	128.0	377.0	103.5	124.3	113.9	373.9
0.0010	106.4	127.3	375.9	102.8	123.6	113.1	372.9
0.0020	105.5	126.2	375.3	101.8	122.5	112.1	371.4
0.0050	103.7	124.3	372.6	99.97	120.4	110.0	371.0
0.0100	101.9	122.4	369.3	98.07	118.1	107.8	365.0
0.0200	99.6	119.9	365.5	95.57	115.1	105.1	364.0
0.0500	95.7	115.7	358.4	91.35	109.8	99.5	353.7
0.1000	92.0	112.0	351.4	87.16	104.7	94.3	346.4
0.2000	87.7	107.9	342.0	82.21	98.7	....	340.0
0.5000	80.9	102.4	327.0	73.99	89.2	77.5	324.0
1.0000	74.3	98.2	301.0	65.81	80.4	67.6	310.0

Normal Conc.	Na_2SO_4	H_2SO_4†	$CaCl_2$	NaOH†	KOH†	NH_4OH	CH_3COOH
0.0000	111.9	.....	117.4	.....	.....	239.00	350.00
0.0001	109.3	.....	115.2	.....	.....	66.00	107.00
0.0005	106.7	.....	113.3	.....	.....	38.00	57.00
0.0010	105.1	361.0	112.0	.....	234.0	28.00	41.00
0.0020	103.5	351.0	110.1	204.5	233.0	20.60	30.20
0.0050	99.8	330.0	106.7	.....	230.0	13.20	20.00
0.0100	95.7	308.0	103.4	203.4	228.0	9.60	14.30
0.0200	.....	286.0	99.4	.....	225.0	7.10	10.40
0.0500	83.6	253.0	93.3	199.0	219.0	4.60	6.48
0.1000	77.1	225.0	88.2	195.4	213.0	3.30	4.60
0.2000	70.0	214.0	82.8	.....	206.0	2.30	3.24
0.5000	.....	205.0	74.9	174.1	197.0	1.35	2.01
1.0000	.....	198.0	67.6	157.0	184.0	0.89	1.32

* Noyes and Falk, Jour. Am. Chem. Soc., **34**, 461 (1912).
† Landolt and Börnstein Tabellen.

The Law of Kohlrausch. The electrical conductance of solutions was systematically investigated by Kohlrausch who showed that the limiting value of the equivalent conductance, which may be represented by Λ_0, is different for different electrolytes, and may be considered as the sum of two independent factors, one of which refers to the cation and the other to the anion. This experimental result is commonly known as the law of Kohlrausch.

The limiting value of the equivalent conductance is reached when the molecules are completely broken down into ions, and, under these conditions, the whole of the electrolyte participates in conducting the current. The accompanying table, giving the equivalent conductances at infinite dilution of several binary electrolytes, illustrates the truth of the law of Kohlrausch.

EQUIVALENT CONDUCTANCES AT INFINITE DILUTION
Temp. 18°

	K	Na	Li	NH_4	H	Ag
Cl	130	108	98	130	378	.....
NO_3	126	105	.....	.....	375	116
OH	238	217	.....	.....	.....	.....
ClO_3	119	.....	.....	.....	.....	109
$C_2H_3O_2$	99	78	.....	.....	.....	89

The differences between two corresponding sets of numbers in the same vertical column, or between any two corresponding sets of numbers in the same horizontal row, will be found to be nearly equal. This could only occur when the limiting conductance represents the sum of two entirely independent quantities.

Each ion invariably carries the same charge of electricity, and moves with its own velocity, quite independent of the nature of its companion ion. Therefore, at infinite dilution, we have

$$\Lambda_0 = l_c + l_a, \tag{6}$$

in which l_c and l_a are the equivalent conductances of the ions of the electrolyte at infinite dilution. From this it follows, that

$$n_a = \frac{l_a}{l_c + l_a} = \frac{l_a}{\Lambda_0}, \tag{7}$$

and

$$n_c = \frac{l_c}{l_c + l_a} = \frac{l_c}{\Lambda_0}; \tag{8}$$

or

$$l_a = n_a \Lambda_0, \tag{9}$$

and

$$l_c = n_c \Lambda_0. \tag{10}$$

Thus, the equivalent conductance of silver nitrate at infinite dilution, at 18°, is 115.5, while $n_a = 0.518$ and $n_c = 0.482$; therefore,

$$l_a = 0.518 \times 115.5 = 59.8,$$

and

$$l_c = 0.482 \times 115.5 = 55.7;$$

or, one gram-equivalent of NO_3' ions possesses a conductance of 59.8, when placed between electrodes one centimeter apart, and large enough to contain between them the entire volume of solution in which the NO_3' ions exist. Under the same conditions, one gram-equivalent of $Ag^{\cdot}$ ions has a conductance equal to 55.7.

The values of the ionic conductances, at infinite dilution, remain constant in all solutions in the same solvent at the same temperature, so that it is possible to calculate the equivalent conductance for any substance at infinite dilution.

In the subjoined table are given the ionic conductances of various ions at 18° and infinite dilution, together with their temperature coefficients.

IONIC CONDUCTANCES AT INFINITE DILUTION

Temp 18°

Ion	l	Temp. Coeff.	Ion	l	Temp. Coeff.
$Li^{\cdot}$	33.07	0.0265	ClO_3'	54.95	0.0215
$Na^{\cdot}$	43.23	0.0244	IO_3'	33.83	0.0234
$K^{\cdot}$	64.30	0.0217	NO_3'	61.71	0.0205
$Rb^{\cdot}$	67.6	0.0214	$H^{\cdot}$	313.0	.....
$Cs^{\cdot}$	67.56	0.0212	OH'	174.0	.....
$NH_4^{\cdot}$	64.5	0.0222	$\frac{1}{2}\,Zn^{\cdot\cdot}$	45.6	0.0251
$Tl^{\cdot}$	65.5	0.0215	$\frac{1}{2}\,Mg^{\cdot\cdot}$	45.0	0.0256
$Ag^{\cdot}$	53.9	0.0229	$\frac{1}{2}\,Ba^{\cdot\cdot}$	55.0	0 0238
Cl'	65.34	0.0216	$\frac{1}{2}\,Pb^{\cdot\cdot}$	61.0	0.0243
Br'	67.41	0.0215	$\frac{1}{2}\,SO_4''$	68.0	0.0227
I'	66.35	0.0213	$\frac{1}{2}\,CO_3''$	70.0	0.0270

In the case of weak electrolytes, the value of Λ_0 cannot be determined directly from conductance measurements, since the solution becomes so dilute before the limiting value of the conductance is reached that accurate measurements of the specific conductance are impossible. However, the law of Kohlrausch enables us to overcome this difficulty. Thus, the value of Λ_0 for acetic acid must be equal to the sum of the conductances of the $H^{\cdot}$ and CH_3COO' ions. The conductance of the $H^{\cdot}$ ion at 18° is 313, according to the preceding table, while the value of the conductance of sodium acetate at infinite dilution is 78.1 at 18°. Since the ionic conductance of the $Na^{\cdot}$ ion is 43.23 at 18°, it fol-

lows that the conductance of the CH_3COO' ion must be 78.1 − 43.23 = 34.87. Therefore, for acetic acid, we have

$$\Lambda_0 = l_c + l_a = 313 + 34.87 = 347.87 \text{ at } 18°.$$

Bredig* showed that the ionic conductance of elementary ions is a periodic function of the atomic weight. Since the atomic number† rather than the atomic weight is now known to be the fundamental property of the atom, the ionic conductances of the atoms studied by Bredig are plotted against their atomic numbers instead of their atomic weights in Fig. 133. A glance at the curve shows the periodic nature of the relation.

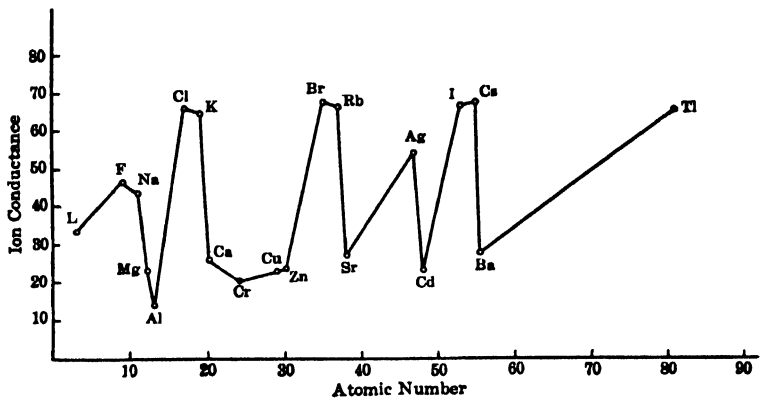

Fig. 133

Conductance and Ionization. We have already seen that solutions of strong acids, strong bases and salts exert abnormally great osmotic pressures. According to the molecular theory, this abnormal osmotic activity has been ascribed to the presence in the solutions of a greater number of dissolved particles than would be anticipated from the simple molecular formulas of the solutes. The ratio of the observed to the theoretical osmotic pressure was represented, according to van't Hoff, by the factor "i."

That there is an intimate connection between electrical conductance and abnormal osmotic activity, is shown by the fact, discovered by Arrhenius in 1887, that only those solutions conduct the electric current which exert abnormally high osmotic pressures. It had already been pointed out by Kohlrausch, that the

* Zeit. phys. Chem., 13, 242 (1894).

† For definition of the term "atomic number" see p. 684.

equivalent conductance of a solution increases initially with the dilution, and then, ultimately, becomes constant. Arrhenius explained this behavior by assuming that the molecules of the solute undergo dissociation into ions. The degree of dissociation increases with the dilution until finally, when the equivalent conductance has reached its maximum value, the molecules of solute become completely broken down into ions. According to the theory of electrolytic dissociation, the conductance of a solution is dependent upon the number of ions present in the solution, upon the magnitude of their charges, and upon their velocities. Since the electric charges carried by equivalent amounts of the ions of different electrolytes are equal, and since the velocities of the ions for the same electrolyte are practically independent of the dilution of the solution, it follows that the increase in equivalent conductance with dilution must depend almost wholly upon the increase in the number of ions present.

The equivalent conductance of an electrolyte at infinite dilution has been shown to be

$$\Lambda_0 = l_c + l_a,$$

and, therefore, the equivalent conductance at any dilution v, must be

$$\Lambda = \alpha\,(l_c + l_a),$$

where α is the degree of dissociation of the electrolyte. Dividing the second equation by the first, we obtain,

$$\alpha = \frac{\Lambda}{\Lambda_0}. \tag{11}$$

This equation enables us to calculate the degree of ionization of an electrolyte at any concentration, provided we know the conductance of its solution at the given concentration, and also its conductance, at infinite dilution. It should be borne in mind, that equation (11) was derived on the assumption, that in any solution the velocities of the anions and cations are the same as at infinite dilution. Since the solutions of many electrolytes are known to possess high viscosities, it is more than probable that in these solutions the ions encounter very appreciable resistance, in consequence of which their velocities become more and more reduced as the concentration is increased. If we assume that Stokes' law is applicable to the motion of an ion through a solution, that is, that the equivalent conductance of an ion is inversely

proportional to the viscosity of the medium through which it moves, it follows, that equation (11) may be written in the form,

$$\alpha = \frac{\Lambda}{\Lambda_0} \cdot \frac{\eta}{\eta_0}, \qquad (12)$$

where η and η_0 are the viscosities of the solution and solvent, respectively. In some cases it has been found, that the values calculated by means of equation (12) are in better agreement with the results obtained from freezing-point measurements than are the values calculated by means of equation (11); in other cases, the latter equation is found to give the better results. At the present time it may be fairly assumed that the simpler equation gives a correct measure of the degree of ionization of all uni-univalent electrolytes in dilute solution.

Ionization of Salts, Acids and Bases. The values of the conductance ratio, Λ/Λ_0, for salts of the same general type, are practically identical at the same equivalent concentrations. This is clearly shown by the accompanying table, compiled by Randall,* giving the ionization values of typical salts of various valence types at 18°.

VALUES OF THE CONDUCTANCE RATIO, Λ/Λ_0, FOR TYPICAL SALTS

Temp. 18°

Salt	Concentration (gram-mols per liter)								
	0.0001	0.0002	0.0005	0.001	0.002	0 005	0.01	0.05	0.10
KCl	99.2	99.0	98.5	97.9	97.1	95.6	94.1	88.9	86.0
$LiIO_3$	99.1	98.7	97.9	97.0	95.8	93.6	91.2	83.4	78.9
$MgCl_2$	98.4	97.8	96.7	95.5	93.9	91.0	88.3	80.3	76.5
$Ba(NO_3)_2$	98.4	97.8	96.7	95.3	93.4	89.8	86.1	74.4	67.9
Tl_2SO_4	....	....	96.4	94.8	92.4	88.2	83.7	69.4	62.5
$PbCl_2$	....	....	96.0	94.3	91.7	86.5	80.8	62.7	....
$K_4Fe(CN)_6$	....	....	....	....	85.9	....	71.2	59.1	....
$CuSO_4$	96.1	94.4	90.5	86.2	80.4	70.9	62.9	....	....

In the case of uni-univalent and bi-bivalent salts, the conductance ratio undoubtedly affords a true measure of the degree of ionization, because salts belonging to these types dissociate directly

* Jour. Am. Chem. Soc., 38, 788 (1916).

into the ions corresponding to the equivalent conductance at infinite dilution. As has been pointed out in a previous chapter, salts of higher types dissociate in stages, giving rise to intermediate ions. For example, a bi-univalent salt, such as $CaCl_2$, dissociates in the following manner:

$$\text{(a)}\ CaCl_2 \rightarrow CaCl^{\cdot} + Cl',$$
$$\text{(b)}\ CaCl^{\cdot} \rightarrow Ca^{\cdot\cdot} + Cl'.$$

At infinite dilution, when ionization is complete, only two species of ions will be present, but at any finite concentration there will always be three ionic species present in unknown relative amounts. Obviously, equation (11) cannot be employed to calculate the degree of ionization when more than two species of ions are present. An indirect method for the determination of the degree of ionization of certain salts which yield intermediate ions has been developed by Harkins.*

With very few exceptions, all salts are highly ionized in dilute solution. Among the most noteworthy exceptions are the mercury halides and cadmium chloride; in 0.1 molar solution, the degree of ionization of the former is only 0.1 per cent, while that of the latter is 45 per cent. No satisfactory explanation has been advanced to account for these anomalies.

While, in equivalent concentrations, salts of the same ionic type are ionized to practically the same extent, the degree of ionization of acids and bases is found to vary in a most surprising manner. This is apparent from the following table, in which the degree of ionization of several typical acids and bases is recorded.

DEGREE OF IONIZATION OF ACIDS AND BASES AT 18°

Concentration	$\alpha = \frac{\Lambda}{\Lambda_0}$				
	HCl	HNO_3	$HC_2H_3O_2$	KOH	NH_4OH
0.001	99.0	99.0	11.7	....	11.7
0.002	98.6	98.6	8.6	98.0	8.6
0.005	98.1	....	5.7	97.5	5.5
0.010	97.2	96.9	4.1	96.3	4.0
0.020	95.7	....	3.0	93.9	3.0
0.050	94.4	93.8	1.8	92.5	1.9
0.100	92.0	92.0	1.3	91.0	1.4

* Jour. Am. Chem. Soc., 33, 1868 (1911).

Absolute Velocity of the Ions. Thus far we have considered only the relative velocities and conductances of uni-univalent ions; we now proceed to the consideration of their absolute velocities in centimeters per second.

Let I amperes of electricity be passed through a centimeter cube of a solution of a uni-univalent electrolyte. If the solution contains C gram-equivalents of electrolyte per liter, the quantity of electricity carried by either the cation or the anion will be $\left(\frac{C\alpha}{1000}\right)F$, where α is the degree of ionization, and where $F = 96{,}500$ coulombs. Since the total quantity of electricity transported across a given section of a solution of an electrolyte by its ions is equal to the sum of the number of equivalents carried by the cations and the anions moving in opposite directions, it follows, that

$$I = \left(\frac{C\alpha}{1000}\right)(U + V)\,F, \tag{13}$$

where U and V are the ionic velocities for unit potential gradient. But by Ohm's law, $I = E/R = EL$, hence, equation (13) becomes

$$EL = \left(\frac{C\alpha}{1000}\right)(U + V)\,F, \tag{14}$$

or, for a potential gradient of 1 volt per centimeter,

$$L = \left(\frac{C\alpha}{1000}\right)(U + V)\,F. \tag{15}$$

Substituting Λ/Λ_0 for α, in equation (15), and remembering that $\frac{C\Lambda}{1000} = L$, we have

$$\Lambda_0 = (U + V)\,F. \tag{16}$$

By means of this equation, the velocities of the ions, expressed in centimeters per second, can be calculated, provided that the corresponding transference numbers are known. For example, the equivalent conductance of a 0.0001 molar solution of potassium chloride, at 18°, is 128.9; the total velocity of the two ions is then,

$$\frac{130}{96{,}500} = 0.001347 \text{ cm. per sec.}$$

This total velocity is made up of the two individual ionic velocities. The transference numbers of the two ions, $K^{\cdot}$ and Cl', are respec-

tively 0.496 and 0.504. Hence, the absolute velocities of the ions, expressed in centimeters per second, in a .0001 molar solution of potassium chloride, at 18°, are as follows:

$$U = 0.001347 \times 0.496 = 0.00067 \text{ cm. per sec.},$$

and

$$V = 0.001347 \times 0.504 = 0.00068 \text{ cm. per sec.}$$

The absolute velocities of some of the more common ions, at 18°, are given in the following table.

ABSOLUTE IONIC VELOCITIES

Ion.	Velocity.	Ion.	Velocity.
	cm. per sec.		cm. per sec.
$K^{\cdot}$	0.00066	$H^{\cdot}$	0.00320
$NH_4^{\cdot}$	0.00066	Cl'	0.00069
$Na^{\cdot}$	0.00045	NO_3'	0.00064
$Li^{\cdot}$	0.00036	ClO_3'	0.00057
$Ag^{\cdot}$	0.00057	OH'	0.00181
Cr_2O_7''	0.000473	$Cu^{\cdot\cdot}$	0.00031

The velocities of certain ions have been determined directly. Thus, the velocity of the hydrogen ion was measured by Lodge * in the following manner: — The tube B, Fig. 134, 40 cm. long and

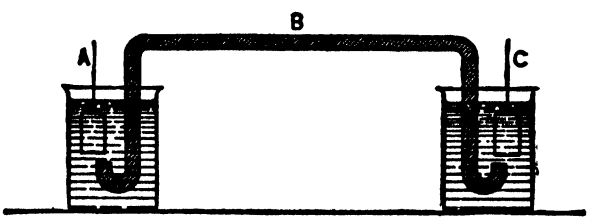

Fig. 134

8 cm. in diameter, was graduated and bent at right angles at the ends. This was filled with an aqueous solution of sodium chloride in gelatine, colored red by the addition of an alkaline solution of phenolphthalein. When the contents of the tube had gelatinized, the tube was placed horizontally, connecting two beakers filled with dilute sulphuric acid, as shown in the diagram. A current of electricity was passed from one electrode A to the other electrode C. The hydrogen ions from the anode vessel travelled

* Brit. Assoc. Report, p. 393 (1886).

through the tube toward the cathode, discharging the red color of the phenolphthalein. By observing the rate at which the color was discharged, the velocity of the hydrogen ion under a known potential gradient was determined. The observed and calculated values agree excellently. It was shown that the velocity of the hydrogen ion suffers almost no retardation from the high viscosity of the gelatine solution.

Whetham,* in his experiments on ionic velocity, employed two solutions, one of which possessed a colored ion, the motion of the latter being observed and its velocity determined under unit potential gradient. For example, consider the boundary line between two equally dense solutions of the electrolytes, AC and BC, C being a colorless, and A a colored ion. When a current passes through the boundary between the two electrolytes, the anion, C, will migrate toward the positive electrode, while the two cations, A and B, will migrate toward the negative electrode, and the color boundary will move with the current, its speed being equal to that of the colored ion, A. In this manner Whetham measured the absolute velocities of the ions, Cu'', Cr_2O_7'', and Cl'.

Ionic velocities have also been determined by Steele,† who observed the change in the index of refraction of the solution as the ions migrated. The accompanying table gives a comparison of the calculated and observed velocities of some of the ions.

ABSOLUTE IONIC VELOCITIES

Ion.	Velocity (obs.).	Velocity (calc.).
	cm. per sec.	cm. per sec.
$H^{\cdot}$	0.0026	0.0032
$Cu^{\cdot\cdot}$	0.00029	0.00031
Cl'	0.00058	0.00069
Cr_2O_7''	0.00047	0.000473

Temperature Coefficient of Conductance. When the temperature of a solution of an electrolyte is raised, the equivalent conductance usually increases. The increase in conductance is due, not to an increase in the ionization, but to the greater velocity of the ions. According to Kohlrausch, the relation between con-

* Phil. Trans. A., 184, 337 (1893); 196, 507 (1895).

† Phil. Trans. A., 198, 105 (1902).

ductance and temperature may be expressed approximately by the following equation,

$$\Lambda_t = \Lambda_{18°} \{1 + \beta (t - 18)\},$$

where β is the temperature coefficient, or change in conductance for 1° C. Solving the equation for β, we have

$$\beta = \frac{\Lambda_t - \Lambda_{18°}}{\Lambda_{18°} (t - 18)}. \tag{17}$$

The temperature coefficients of several of the more common electrolytes are given in the accompanying table.

TEMPERATURE COEFFICIENTS OF CONDUCTANCE

Electrolyte.	Temperature Coefficient.
Nitric acid	0.0163
Sulphuric acid	0.0164
Hydrochloric acid	0.0165
Potassium hydroxide	0.0190
Potassium nitrate	0.0211
Potassium iodide	0.0212
Potassium bromide	0.0216
Potassium chlorate	0.0216
Silver nitrate	0.0216
Potassium chloride	0.0217
Ammonium chloride	0.0219
Potassium sulphate	0 0223
Copper sulphate	0.0225
Sodium chloride	0.0226
Sodium sulphate	0.0234
Zinc sulphate	0.0250

The temperature coefficient of conductance is not, however, a simple linear function of the temperature. The following empirical equations, expressing equivalent conductance at infinite dilution and at any temperature t, in terms of the conductance at 18°, have been derived by Kohlrausch:

$$\Lambda_{0t} = \Lambda_{0\ 18°} \{1 + \alpha (t - 18) + \beta (t - 18)^2\}, \tag{18}$$

and

$$\beta = 0.0163 (\alpha - 0.0174). \tag{19}$$

When the values of $\Lambda_{0\ 18°}$, α, and β, as determined for a large number of electrolytes, are substituted in the above equation, he showed that Λ_{0t} becomes equal to zero at a temperature approx-

imating to −40°. Kohlrausch suggested that each ion moving through the solution carries with it an " atmosphere " of solvent, and that the resistance offered to the motion of the ion is simply the frictional resistance between masses of pure water. This view is in harmony with the solvate theory discussed in an earlier chapter. Washburn * has calculated the degree of ionic hydration for several ions. He finds, for example, that the hydrogen ion carries with it 0.3 molecule of water, while the lithium ion is hydrated to the extent of 4.7 molecules of water.

Conductance at High Temperatures and Pressures. The conductance of several typical electrolytes, at temperatures ranging from that of the room up to 306°, have been measured by A. A. Noyes and his co-workers.† These measurements were carried out in a conductance cell especially constructed to withstand high pressures. The results show that the values of Λ_0, for binary electrolytes, tend to become equal with rise of temperature. This may be taken as an indication of the fact that the ionic velocities tend to become equal as the temperature rises. The conductance of ternary electrolytes increases uniformly with the temperature, and attains values which are considerably greater than those reached by binary electrolytes. This is what might be expected, since if an ion is bivalent, as in a ternary electrolyte, the driving force must be greater, in consequence of which the ion must move faster, and the conductance will increase correspondingly.

The temperature coefficient of conductance for binary electrolytes is greater between 100° and 156°, than below or above these temperatures. The temperature coefficients of ternary electrolytes increases uniformly with rising temperature. In the case of acids and bases, the rate of increase in conductance steadily diminishes as the temperature rises. The ionization decreases regularly with rise in temperature, the temperature coefficient of ionization being small between 18° and 100°.

The effect of pressure on conductance was studied by Fanjung.‡ He found that the conductance increases slightly with increasing pressure. This result he interprets as being due to increased ionic velocity, rather than to an increase in the number of ions present in the solution.

* Jour. Am. Chem. Soc., 30, 322 (1909).

† Publication of Carnegie Institution, No. 63.

‡ Zeit. phys. Chem., 14, 673 (1894).

The Conductance of Pure Liquids. In general, the conductance of pure liquids is small. Thus, the specific conductance of pure water, at 18°, is approximately 0.04×10^{-6} reciprocal ohms and, as Walden* has shown, the specific conductance of a number of other solvents is of the same order as that for water. Mixtures of two liquids, each of which is practically non-conducting, may have a conductance differing but little from that of the two com-

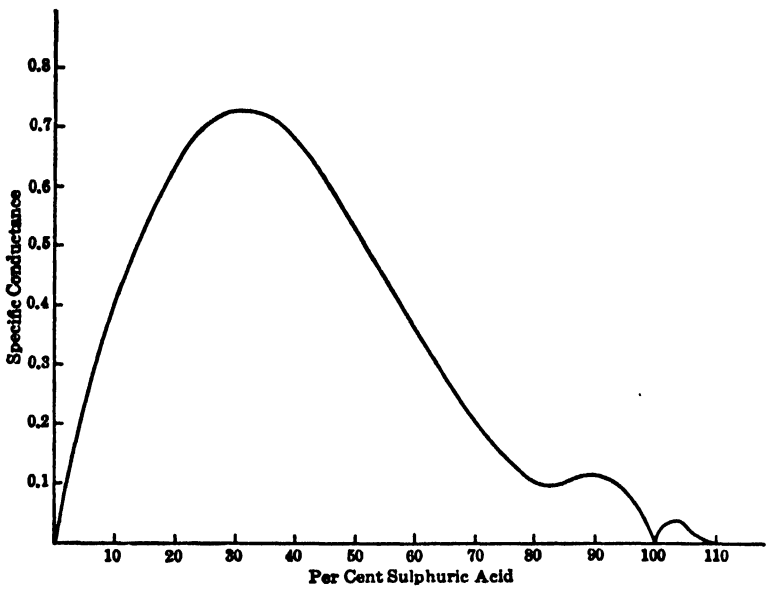

Fig. 135

ponents; or, the mixture may have a very high conductance. For example, the conductance of a mixture of water and ethyl alcohol is of the same order of magnitude as that of the two components, while on the other hand, a mixture of water and sulphuric acid, each of which, in the pure state, is practically a non-conductor, has great conducting power. The variation of the specific conductance of mixtures of water and sulphuric acid is represented graphically in Fig. 135, concentration being plotted on the axis of abscissæ and specific conductance on the axis of ordinates. It appears, that as the concentration of the sulphuric acid increases, the specific conductance of the mixture increases until 30 per cent

* Zeit. phys. Chem., 46, 103 (1903).

of acid is present, beyond which point it gradually diminishes. When pure sulphuric acid is present, the value of the specific conductance is practically zero. On dissolving sulphur trioxide in the pure acid, the specific conductance increases slightly to a maximum, and then falls rapidly to zero. There is a minimum in the curve corresponding to about 85 per cent of acid, a concentration which corresponds almost exactly with the hydrate, $H_2SO_4 \cdot H_2O$. Why some liquid mixtures should have marked conducting power and others hardly any, it is difficult to explain. Many fused salts, such as silver nitrate and lithium chloride, are excellent conductors and are thus exceptions to the general rule, that pure substances, belonging to the second class of conductors, possess little conducting power.

Conductance of Fused Salts. While solid salts are exceedingly poor conductors of electricity, yet as the temperature is raised their conductance increases, until, at their melting-points, they become good conductors. The specific conductance of a fused salt may even exceed the specific conductance of the most concentrated aqueous solutions, but owing to its high concentration, the equivalent conductance is much less. The following table gives the specific and equivalent conductance of fused silver nitrate.

Temperature, degrees.	Sp. Cond.	Equiv. Cond.
218 (melt.-pt.)	0.681	29.2
250	0.834	36.1
300	1.049	46.2
350	1.245	55.4

The specific conductance of a 60 per cent aqueous solution of silver nitrate, at 18°, is 0.208 reciprocal ohm.

If the salts are impure the conductance is raised, the effect of impurities being apparent even before the salts have reached their melting-points. This is analogous to the behavior of solutions, and suggests that the impurity functions in the salt mixture as a dissolved solute.*

* For a complete treatment of fused electrolytes, the student is advised to consult, "Die Elektrolyse geschmolzener Salze," by Richard Lorenz.

Conductance of Non-aqueous Solutions. A large amount of interesting and important work has been done in recent years on the electrical conductance of solutions in non-aqueous solvents. In general, those liquids which yield conducting solutions are themselves also conductors of electricity. When the solvent is an inorganic substance, such as ammonia, sulphur dioxide or hydrocyanic acid, the conductance is comparable with that of aqueous solutions, but when the solvent is an organic compound, the conductance is almost always very much less than that of the corresponding aqueous solution. The following examples will serve to illustrate the wide variation in the conductance of solutions of silver nitrate in different solvents.

CONDUCTANCE OF SILVER NITRATE IN DIFFERENT SOLVENTS*
Temp. 25°

Silver Nitrate in Ethyl Alcohol		Silver Nitrate in Methyl Alcohol	
c	$\Lambda_{25}°$	c	$\Lambda_{25}°$
0.1	10.81	0.1	36.64
0.01	22.06	0.01	68.75
0.0078	23.72	0.006	74.88
0.003	28.14	0.003	83.14
0.001	34.95	0.0012	87.30
0.00056	37.79	0.001	90.10
0.0003	38.52	0.0003	87.82
0.0001	40.71	0.0001	73.23

Silver Nitrate in Acetone		Silver Nitrate in Aniline	
c	$\Lambda_{25}°$	c	$\Lambda_{25}°$
0.01	10.51	0.1	0.666
0.003	11.39	0.01	0.327
0.001	15.43	0.003	0.436
0.0003	20.78	0.001	0.678
0.00016	25.60	0.0003	1.082
0.0001	28.06	0.0001	1.651

Silver Nitrate in Pyridine

c	$\Lambda_{25}°$	c	$\Lambda_{25}°$
0.1	24.80	0.0003	66.14
0.01	33.85	0.0001	73.50
0.003	43.68	0.00006	75.82
0.001	54.13		

The conductance of alcoholic solutions is found to diminish as the molecular weight of the solvent increases. In fact, in any

* Gibbons & Getman, Jour. Am. Chem. Soc., 36, 1640 (1914).

homologous series whose members form conducting solutions, the conductance decreases as the number of carbon atoms in the solvent increases.

A study of solutions in anhydrous formic acid has recently been made by Schlesinger,* who finds that these solutions are more nearly normal in their behavior than the corresponding aqueous solutions. Solutions of potassium iodide in acetone conduct better than the corresponding solutions in methyl and ethyl alcohols, whereas, the conductance of lithium chloride and silver

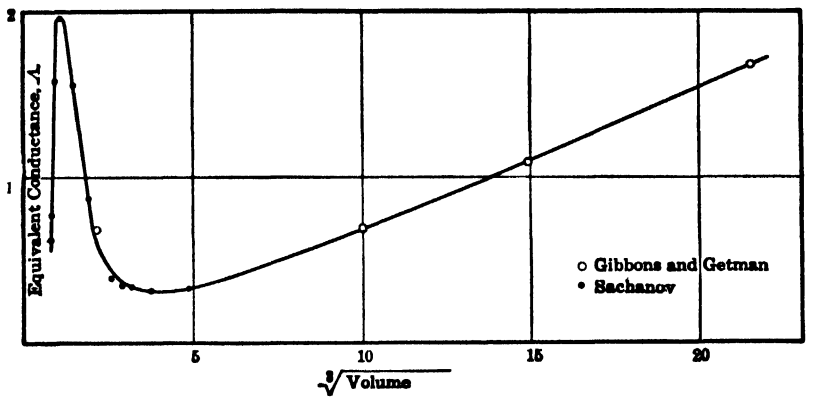

Fig. 136

nitrate in the latter solvents is much greater than in acetone. Solutions in pyridine are found to conduct well, while solutions in the analogous solvents, piperidine and quinoline, are to be classed among poor conductors. Such irregularities in the conductance of the same electrolyte in different non-aqueous solvents are found to be quite general.

In nearly every instance, the equivalent conductance increases with the dilution, as in the case of aqueous solutions. There are numerous exceptions to this rule, however, a notable example being that of silver nitrate in aniline, the conductance curve of which is shown in Fig. 136.

The molecular weight of the solute in dilute aqueous solutions, as determined by the freezing-point and boiling-point methods, is usually much less than the simple formula-weight. In non-aqueous solutions, the reverse is quite frequently found to be true.

* Jour. Am. Chem. Soc., 41, 1923 (1919).

Owing to the difficulty in determining Λ_0 with sufficient accuracy, it is impossible, in most cases, to calculate the degree of ionization of an electrolyte in non-aqueous solution. In those few cases where it has been possible to estimate the value of Λ_0, the degree of ionization, thus calculated, has rarely been found to agree with that calculated from freezing-point or boiling-point measurements.

While solutions of electrolytes in the lower alcohols resemble aqueous solutions very closely, this resemblance is found to decrease rapidly as the molecular weight of the alcohol increases. Solutions of electrolytes in almost all other non-aqueous solvents do not appear to undergo dissociation in the same manner as in aqueous solutions. In fact, it is known that the molecules of electrolytes tend to become polymerized in non-aqueous solutions. These polymerized molecules may be formed by the union of two or more molecules of the solute, or by the combination of one or more molecules of the solute with one or more molecules of the solvent. Undoubtedly, it is to the presence of such aggregates in certain non-aqueous solutions that the decrease in their conductance on dilution is to be ascribed.

Ionizing Power of Solvents. Both Thomson* and Nernst† pointed out, that if the forces which hold the atoms in the molecule are of electrical origin, then those liquids which possess large dielectric constants should have correspondingly great ionizing power. This is a direct consequence of Coulomb's law of electrostatic attraction, which may be expressed by the equation,

$$f = \frac{q_1 q_2}{K d^2}, \tag{20}$$

in which q_1 and q_2 denote the electric charges, d the distance between them, f the force of attraction and K the dielectric constant. Obviously the larger K becomes, the smaller will be the value of f; i.e., the more likely the molecule will be to break down into ions. That the above relation is approximately true may be seen from the following table.

Dutoit and Aston‡ have suggested that there is a connection between the ionizing power of a solvent and its degree of associa-

* Phil. Mag., 36, 320 (1893).
† Zeit. phys. Chem., 13, 531 (1894).
‡ Compt. rend., 125, 240 (1897).

tion, while Dutoit and Friderich* conclude from their experiments that the values of Λ_0 for a given electrolyte dissolved in different solvents, are a direct function of the degree of association, and an inverse function of the viscosity of the solvents. Water and the alcohols furnish good illustrations of the truth of this generalization.

DIELECTRIC CONSTANTS

Solvent.	*K.*	Ionising Power.
Benzene	2.3	Extremely weak
Ethyl ether	4.1	Weak
Ethyl alcohol	25	Fairly strong
Formic acid	62	Strong
Water	80	Very strong
Hydrocyanic acid	96	Very strong

Application of Conductance Measurements. (a) *The Dissociation of Water.* Water behaves as a very weak binary electrolyte, dissociating according to the equation,

$$H_2O \rightleftarrows H^{\cdot} + OH'.$$

The specific conductance of water, purified with the utmost care, has been determined by Kohlrausch and Heydweiller.† Their results are given in the following table: —

SPECIFIC CONDUCTANCE OF WATER

Temperature, degrees.	Specific Conductance $\times 10^8$
0	0.014
18	0.040
25	0.055
34	0.084
50	0.170

The conductance of pure water, at 0°, is so small that one millimeter of it has a resistance equal to that of a copper wire of the same cross-section and 40,000,000 kilometers in length, or in

* Bull. Soc. Chim. [3], 19, 321 (1898).

† Zeit. phys. Chem., 14, 317 (1894).

other words, long enough to encircle the earth one thousand times. Knowing the specific conductance of water, its degree of dissociation can easily be calculated. The ionic conductances of the two ions of water, at 18°, are as follows: — $H^{\cdot}$ = 313, and OH' = 174. Therefore, the maximum equivalent conductance of water should be,

$$\Lambda_0 = 313 + 174 = 487.$$

The equivalent conductance, at 18°, of a liter of water between electrodes 1 cm. apart is, according to the data of Kohlrausch,

$$0.04 \times 10^{-6} \times 10^{3} = 0.04 \times 10^{-3};$$

therefore,

$\frac{0.04 \times 10^{-3}}{487} = 0.8 \times 10^{-7} = c$, the concentration of the ions, $H^{\cdot}$ and OH', in mols per liter at 18°.

(b) *Solubility of Difficultly Soluble Salts.* In a saturated solution of a difficultly soluble salt, the solution is so dilute that, in general, we may assume complete ionization, or $\Lambda = \Lambda_0$.

When this is the case, we have

$$L_{\text{solution}} - L_{H_2O} = L,$$

and

$$\Lambda = \Lambda_0 = \frac{1000\,L}{C}.$$

Hence,

$$C = \frac{1000\,L}{\Lambda_0},$$

where C denotes the concentration in gram-equivalents per liter. Thus, Böttger found for a saturated solution of silver chloride, at 20°, $L' = 1.374 \times 10^{-6}$. Deducting the specific conductance of the water at this temperature, we have

$$L = 1.374 \times 10^{-6} - 0.044 \times 10^{-6} = 1.33 \times 10^{-6}.$$

Since the value of Λ_0, at 20°, for silver chloride, determined from the table of ionic conductances, is 119.2, we have

$$m = \frac{1000 \times 1.33 \times 10^{-6}}{119.2} = 1.12 \times 10^{-5} \text{ gr.-equiv. AgCl per liter.}$$

(c) *The Basicity of Organic Acids.* The Ostwald dilution law holds strictly for all monobasic organic acids, and also for poly-

basic organic acids, which are less than 50 per cent ionized. The neutral salts of these acids, however, are much more highly ionized, and the difference in conductance between two dilutions of a neutral salt of a polybasic acid is greater than the difference in conductance between the same dilutions of a neutral salt of a monobasic acid.

Ostwald* has shown that it is possible to estimate the basicity of an organic acid from the difference in the equivalent conductance of its sodium salt at two different dilutions. As the result of a long series of experiments, he found that the difference between the equivalent conductance of the sodium salt of a monobasic organic acid, at $v = 32$ liters, and at $v = 1024$ liters, is approximately 10 units. Similarly, for a dibasic acid, the difference between the same dilutions is 20 units, and for an n-basic acid the difference is $10\,n$. Hence, to estimate the basicity of an organic acid, the equivalent conductance of its sodium salt, at $v = 32$ liters, and at $v = 1024$ liters, is determined; then, if Δ is the difference between the values of the conductance at the two dilutions, the basicity will be $n = \frac{\Delta}{10}$.

The following table gives the values of Δ and n for the sodium salts of several typical organic acids.

BASICITY OF ORGANIC ACIDS

Acid.	Δ	n
Formic	10.3	1
Acetic	9.5	1
Propionic	10.2	1
Benzoic	8.3	1
Quininic	19.8	2
Pyridine-tricarboxylic (1, 2, 3)	31.0	3
Pyridine-tricarboxylic (1, 2, 4)	29.4	3
Pyridine-tetracarboxylic	41.8	4
Pyridine-pentacarboxylic	50.1	5

(d) *Determination of Hydrolysis.* The degree of hydrolysis can be determined experimentally in several different ways. A very convenient method is that based upon measurements of electrical conductance. When a salt reacts hydrolytically

* Ostwald. Zeit. phys. Chem. **1**, 105 (1887); **2**, 902 (1888).

with one mol of water, the limiting value of its equivalent conductance will be $\Lambda_A + \Lambda_B$, where Λ_A and Λ_B denote the equivalent conductances of the acid and base formed. If Λ is the equivalent conductance of the unhydrolyzed salt, and Λ_h is the actual conductance of the salt at the same dilution, then the increase in conductance, corresponding to a degree of hydrolysis, x, will be $\Lambda_h - \Lambda$. The value of Λ may be found by determining the conductance of the salt in the presence of an excess of one of the products of hydrolysis, and deducting from it the conductance of the substance added. If the hydrolysis were complete, the equivalent conductance would be $\Lambda_A + \Lambda_B - \Lambda$ hence we have

$$x = \frac{\Lambda_h - \Lambda}{\Lambda_A + \Lambda_B - \Lambda},$$

all conductances being measured at the same dilution and at the same temperature. The following example will illustrate the use of this equation: — At 25°, the equivalent conductance of an aqueous solution of aniline hydrochloride is 118.6, the dilution being 99.2 liters. The equivalent conductance, in the presence of an excess of aniline, is 103.6, while the equivalent conductance of hydrochloric acid, at the same dilution, is 381. The conductance of pure aniline is so small as to be negligible. Substituting these values in the above equation, we find

$$x = \frac{118.6 - 103.6}{381 - 103.6} = 0.0541.$$

Lundén* has shown how this method may be extended to cases where both acid and base are slightly dissociated.

(e) *Determination of End-points.* The possibility of determining the end-points in titration reactions by means of the conductance method was first pointed out by Kohlrausch† in 1885. Subsequent research by numerous investigators‡ has demonstrated the applicability of the method to a wide variety of reactions.

* Jour. chim. phys., **5**, 145, 574 (1907).

† Kohlrausch, Ann. Phys. Chem., **26**, 225 (1885).

‡ Küster, Grüters and Geibel, Zeit. Anorg. Chem., **42**, 225 (1904); Küster and Grüters, ibid., **35**, 454 (1903); Dutoit, Jour. Chim. Phys., **8**, 12 (1910); Dutoit and Mojoiu, Ibid., **8**, 27 (1910); Van Suchtelen and Itano, Jour. Am. Chem. Soc., **36**, 1793 (1914); Harned, ibid., **39**, 252 (1917); Kolthoff, Zeit. Anal. Chem., **61**, 171, 229, 332, 369, 433 (1922); **62**, 1, 97, 161, 209 (1923).

The conductance of a solution being dependent upon both the concentration and the speed of its ions, it follows that any changes which may occur in either of these factors during a reaction will produce corresponding changes in the electrical conductance of the reaction mixture.

The application of the conductance method to neutralization and precipitation reactions will be briefly outlined.

(1) *Neutralization Reactions.* In the case of the neutralization of a strong acid by a strong base, the conductance of the acid will diminish as its highly mobile hydrogen ions are gradually replaced by the slower moving cations of the base. Since the degree of ionization of the resulting salt is of the same order of magnitude as that of the acid, it follows that the conductance of the acid solu-

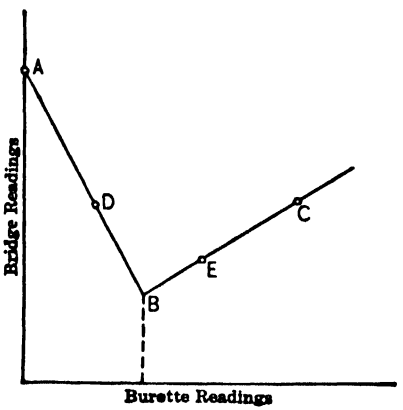

Fig. 137

tion will continue to decrease until the end-point is reached and all of the hydrogen ions have combined with the hydroxyl ions of the base. As soon as an excess of the base is added, however, the conductance will begin to increase corresponding to the increase in the total number of ions, especially to the increase in the number of fast-moving hydroxyl ions.

If the comparison resistance be kept constant, the change in conductance of the acid solution, resulting from the addition of successive portions of base, will be proportional to the bridge readings. Hence, if bridge readings be plotted as ordinates against the corresponding burette readings as abscissæ, a graph resembling

that shown in Fig. 137 will be obtained. The abscissa corresponding to the point B, at which the two rectilinear branches intersect, is the end-point. In order that AB and AC shall be strictly rectilinear it is necessary that the volume of the solution remain constant throughout the titration. Practically this condition is fulfilled if the total volume of the reagent is not more than two per cent of the volume of the solution to be titrated. In other words, the reagent must be concentrated while the solution to be titrated must be dilute. If these conditions be fulfilled, four readings corresponding to the points A, B, C, and D will suffice to determine the end-point in the titration of a strong acid by a strong base.

Among the more important factors governing the accuracy of the method may be mentioned: (1) The degree of ionization of the electrolytes involved; (2) The ionic conductances; (3) Hydrolysis; and (4) Solubility of any precipitates, or the stability of any complexes which may be formed.

The foregoing method has proven of great value in titrating colored or turbid solutions in which the determination of the end-point is often rendered uncertain owing to the masking of the color of the indicator by the color of the solution.

(2) *Precipitation Reactions.* The conductance method may also be applied to the determination of the end-points of reactions involving precipitations; in fact, the method is often superior to the more familiar analytical procedures.

Let 100 cc. of a 0.001 N solution of the compound BA be titrated with a normal solution of the reagent CD, and let the compound DB be precipitated, as indicated by the reaction,

$$BA + CD = BD + CA.$$

If, as in the preceding case, conductances be plotted as ordinates against burette readings as abscissæ, a graph similar to that shown in Fig. 138 will be obtained. Representing the ionic conductances involved in the reaction by Λ_A, Λ_B, Λ_C and Λ_D, the conductance of the original solution will be $0.001\ (\Lambda_B + \Lambda_A)$ and, if the precipitate be assumed to be completely insoluble, the conductance at the equivalent point, B, will be $0.001\ (\Lambda_C + \Lambda_A)$. In like manner, the conductance at the point, C, will be $0.001\ (2\,\Lambda_C + \Lambda_A + \Lambda_D)$.

The tangent of the angle α can readily be derived from the tangents of the adjacent angles FBA and FBC. If now we make $DO = DE = m$, and denote the normality of the original solution by n, it may be shown that

$$\tan \alpha = \frac{-(\Lambda_B + \Lambda_D)m}{m^2 + n^2(\Lambda_C - \Lambda_B)(\Lambda_C + \Lambda_D)}.$$

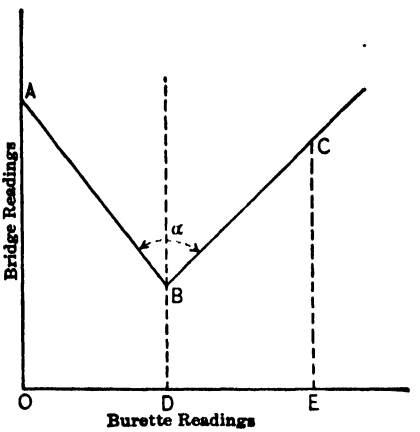

Fig. 138

Dutoit,* who originally derived this relation, pointed out that:

(1) The angle α, and therefore the sharpness of the end-point, is independent of the nature of the anion A.

(2) The angle α increases as Λ_D increases.

(3) The angle α increases as Λ_C increases.

(4) The angle α increases as m increases.

The method just outlined has been applied to various precipitation reactions, such as the precipitation of silver chloride and barium sulphate, as well as to the estimation of magnesium, copper, nickel and cobalt in solutions of the sulphates of these metals.

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* Dutoit, loc. cit., p. 17.

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PROBLEMS

1. An aqueous solution of copper sulphate is electrolyzed between copper electrodes until 0.2294 gram of copper is deposited. Before electrolysis the solution at the anode contained 1.1950 grams of copper, after electrolysis 1.3600 grams. Calculate the transference numbers of the two ions, $Cu^{\cdot\cdot}$ and SO_4''. *Ans.* $n = 0.72$, $1 - n = 0.28$.

2. A solution containing 0.1605 per cent of NaOH was electrolyzed between platinum electrodes. After electrolysis 55.25 grams of the cathode solution contained 0.09473 gram of NaOH, whilst the concentration of the middle portion of the electrolyte was unchanged. In a silver coulometer the equivalent of 0.0290 gram of NaOH was deposited during electrolysis. Calculate the transference numbers of the $Na^{\cdot}$ and OH' ions.

3. In a 0.01 molar solution of potassium nitrate, the transference numbers of the cation and anion are, respectively, 0.503 and 0.497. Find the equivalent conductances of the two ions in this solution, having given that its specific conductance is 0.001044. *Ans.* $l_c = 52.5$, $l_a = 51.9$.

4. The absolute velocity of the $Ag^{\cdot}$ ion is 0.00057 cm. per sec., and that of the Cl' ion is 0.00069 cm. per sec. Calculate the equivalent conductance of an infinitely dilute solution of silver chloride.

5. The equivalent conductance of an infinitely dilute solution of ammonium chloride is 130; the ionic conductances of the ions, OH' and Cl', are 174 and 65.44 respectively. Calculate the equivalent conductance of ammonium hydroxide at infinite dilution. *Ans.* $\Lambda_0 = 238.56$.

6. The equivalent conductance of a molar solution of sodium nitrate at 18° is 66; its conductance at infinite dilution is 105.3. What is the degree of ionization in the molar solution?

7. The specific conductance of a saturated solution of AgCN at 20° is 1.79×10^{-6} and the specific conductance of water at the same temperature is 0.044×10^{-6} reciprocal ohms. The equivalent conductance at infinite dilution is 115.5. Calculate the solubility of AgCN in grams per liter.

8. The equivalent conductance, at 18°, of a solution of sodium sulphate containing 0.1 gram-equivalent of salt per liter is 78.4, the conductance

at infinite dilution is 113 reciprocal ohms. What is the value of i for the solution? What is its osmotic pressure?

9. The freezing-point of a 0.1 molar solution of $CaCl_2$ is $-0°.482$. (a) Calculate the degree of ionization (freezing-point constant = 1.89 for one mol per liter). (b) Calculate the degree of ionization from the equivalent conductance at 18°, which is 82.79 reciprocal ohms, whilst the equivalent conductance of $CaCl_2$ at infinite dilution is 115.8 reciprocal ohms. *Ans.* (a) $\alpha = 0.774$, (b) $\alpha = 0.715$.

10. The equivalent conductance of aniline hydrochloride at a dilution of 197.6 liters is 126.7 reciprocal ohms, at 25°. The equivalent conductance of aniline hydrochloride in the presence of an excess of aniline is 106.6; and the equivalent conductance of hydrochloric acid at the same dilution is 415. If the conductance of pure aniline is negligible, calculate the degree of hydrolytic dissociation and the constant of hydrolysis, assuming $\alpha_s = \alpha_s = 1$.

Ans. $x = 6.52$ per cent, $K_h = 2.30 \times 10^{-5}$.

CHAPTER XVI

ELECTROLYTIC EQUILIBRIUM AND HYDROLYSIS

Ostwald's Dilution Law. It has been shown, in preceding chapters, that the law of mass action is applicable to chemical equilibria, in both gaseous and liquid systems. We now proceed to show that it applies equally to electrolytic equilibria. When acetic acid is dissolved in water it dissociates according to the equation,

$$CH_3COOH \rightleftarrows CH_3COO' + H^{\cdot}.$$

Let one mol of acetic acid be dissolved in water, and the solution diluted to v liters, and let α denote the degree of dissociation. Then, the concentration of the undissociated acid is $\frac{1-\alpha}{v}$, and the concentration of each of the ions is $\frac{\alpha}{v}$. Applying the law of mass action, we have

$$\left(\frac{\alpha}{v}\right)^2 = K\left(\frac{1-\alpha}{v}\right),$$

$$\frac{\alpha^2}{(1-\alpha)\,v} = K, \qquad (1)$$

where K is the *equilibrium, or ionization constant.*

This equation expressing the relation between the degree of ionization and dilution, was derived by Ostwald,* and is known as the Ostwald *dilution law.* Since $\alpha = \frac{\Lambda}{\Lambda_0}$, we may substitute this value of α in equation (1), and obtain the expression,

$$\frac{\Lambda^2}{\Lambda_0\,(\Lambda_0 - \Lambda)\,v} = K. \qquad (2)$$

The dilution law may be tested by substituting the value of α, corresponding to any dilution v, in equation (1) and calculating

* Zeit. phys. Chem., 2, 36 (1888); 3, 170 (1889).

the value of the ionization constant, K; the value of α, at any other dilution, may then be calculated, and compared with the value determined by direct experiment. The following table gives the results obtained with acetic acid at 14°.1, K being equal to 0.0000178.

DEGREE OF IONIZATION OF ACETIC ACID

v (in liters).	$\alpha \times 10^2$ (calc.).	$\alpha \times 10^2$ (obs.).
0.994	0.42	0.40
2.02	0.60	0.614
15.9	1.67	1.66
18.1	1 78	1.78
1,500 0	15 0	14.7
3,010.0	20.2	20.5
7,480 0	30.5	30.1
15,000.0	40.1	40.8

As will be seen, the agreement between the observed and calculated values is very close. The table also shows, to how small an extent the molecules of acetic acid are broken down into ions, a molar solution being dissociated less than 0.5 per cent. The dilution law holds for nearly all organic acids and bases, but fails to apply to salts, strong acids, and strong bases. When α is small, the term $(1 - \alpha)$ does not differ appreciably from unity, and equation (1) becomes,

$$\frac{\alpha^2}{v} = K,$$

or

$$\alpha = \sqrt{vK}. \tag{3}$$

On the other hand, when α cannot be neglected, we have, on solving equation (1) for α,

$$\alpha = -\frac{vK}{2} + \sqrt{vK + \frac{v^2K^2}{4}}. \tag{4}$$

The method of derivation indicates that the dilution law is only strictly applicable to binary electrolytes, and therefore, it is improbable that it will hold for electrolytes yielding more than two ions. It has been found, however, that organic acids, whether they are mono-, di-, or polybasic, always ionize as a monobasic acid up to the dilution at which $\alpha = 50$ per cent. This means,

that the dilution law is applicable to polybasic acids up to that dilution at which the acid is 50 per cent ionized.

Strength of Acids and Bases. There are several methods by which the relative strengths of acids can be estimated. A method which has proved of great value is that in which two different acids are allowed to compete for a certain base, the amount of which is insufficient to saturate both of them. Suppose equivalent weights of nitric and dichloracetic acids to be mixed together with sufficient potassium hydroxide to saturate one acid completely. In order to determine the position of the equilibrium represented by the equation,

$$HNO_3 + CHCl_2 \cdot COOK \rightleftarrows CHCl_2 \cdot COOH + KNO_3,$$

we may make use of any method which does not disturb the equilibrium. Since ordinary chemical methods are excluded on this account, it is customary to determine the change in some physical property accompanying the reaction. Thus, Ostwald* found that when one mol of potassium hydroxide is neutralized by nitric acid in dilute solution, the volume increases approximately 20 cc. When one mol of potassium hydroxide is neutralized by dichloracetic acid, however, the increase in volume is 13 cc. It is evident, therefore, that if nitric acid completely displaces dichloracetic acid, as represented by the above equation, the increase in volume will be, $20-13=7$ cc.; if no displacement occurs, however, then the volume will remain constant. He found, that the volume actually increased 5.67 cc. Therefore, the reaction represented by the upper arrow, has proceeded to the extent of $5.67 \div 7 = 80$ per cent. That is to say, in the competition of the two acids for the base, the nitric acid has taken 80 per cent, and the dichloracetic acid has taken 20 per cent, or the relative strengths of the two acids are in the ratio of 80 : 20, or 4 : 1.

The relative strengths of acids can also be determined from their catalytic effect on the rates of certain reactions, such as the hydrolysis of esters or the inversion of cane sugar.

The order of the activity of acids is the same whether measured by equilibrium or kinetic methods. Arrhenius pointed out, that the relative strengths of acids can be readily determined from their electrical conductance. The order of the strengths of acids, as determined by equilibrium and kinetic methods, is the same as

* Jour. prakt. Chem. [2], 18, 328 (1878).

that of their electrical conductances in equivalent solutions. This is well illustrated by the following table in which the three methods are compared, hydrochloric acid being taken as the standard of comparison.

RELATIVE STRENGTH OF ACIDS

Acid.	Method Employed.		
	Equilibrium.	Kinetic.	Conductance.
HCl	100	100	100
HNO_3	100	100	99.6
H_2SO_4	49	53.6	65.1
$CH_2ClCOOH$	9	4.8	4.8
CH_3COOH	.....	0.4	1.4

The results of these, and other experiments, warrant the conclusion that the strength of an acid is determined by the number of hydrogen ions which it yields. It is important to note, that the electrical conductance of an acid is not directly proportional to its hydrogen ion concentration: the relatively high velocity of the H' ion is the cause of the approximate proportionality between these two variables. In the case of a weak acid, the value of the ionization constant may be taken as a measure of its strength. The following table gives the values of the ionization constants, at 25°, for several different acids.

IONIZATION CONSTANTS OF ACIDS

Acid.	Ionisation Constant.
Acetic acid	0.0000180
Monochloracetic acid	0.00155
Trichloracetic acid	1.21
Cyanacetic acid	0.0037
Formic acid	0.000214
Carbonic acid	3040×10^{-10}
Hydrocyanic acid	570×10^{-10}
Hydrogen sulphide	13×10^{-10}
Phenol	1.3×10^{-10}

Since for a weak acid, $\alpha = \sqrt{vK}$, it follows, that for two weak acids at the same dilution, we may write,

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}}, \qquad (5)$$

or, the ratio of the degrees of ionization of the two acids is equal to the square root of the ratio of their ionization constants. Thus, from the data given in the foregoing table for acetic and monochloracetic acids, we have

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{0.000018}{0.00155}} = \frac{1}{9.3},$$

or, the effect of replacing one atom of hydrogen in the methyl group of acetic acid increases the strength of the acid about nine times.

Just as the hydrogen ion concentration of acids determines their strength, so the strength of bases is determined by the concentration of hydroxyl ions. The strength of bases may be estimated by methods similar to those employed in determining the strength of acids. Thus, two different bases may be allowed to compete for an amount of acid sufficient to saturate only one of them; or a catalytic method, developed by Koelichen,* may be used. This method is based upon the effect of hydroxyl ions on the rate of condensation of acetone to diacetonyl alcohol, as represented by the equation,

$$2\,CH_3COCH_3 = CH_3COCH_2C(CH_3)_2OH.$$

In addition to these two methods, the method of electrical conductance is also applicable. The agreement between the results obtained by the three methods is quite satisfactory. The alkali and alkaline earth hydroxides are very strong bases, and are dissociated to about the same extent as equivalent solutions of hydrochloric and nitric acids, while on the other hand, ammonia and many of the organic bases are very weak. The following table gives the ionization constants of several typical bases.

IONIZATION CONSTANTS OF BASES

Base.	Ionization Constant.
Ammonia	0.000023
Methylamine	0.00050
Trimethylamine	0.000074
Pyridine	2.5×10^{-10}
Aniline	1.1×10^{-10}

* Zeit. phys. Chem., 33, 129 (1900).

Mixtures of Two Electrolytes with a Common Ion. Just as the dissociation of a gaseous substance is diminished by the addition of an excess of one of the products of dissociation, so the ionization of weak acids and bases is depressed by the addition of a salt, having an ion common to the acid, or the base. If the degree of ionization of a salt having an ion in common with an acid or a base, is represented by α', and if n denotes the number of molecules of salt present, then the equation of equilibrium of the acid or base will be

$$(n\alpha' + \alpha)\,\alpha = Kv\,(1 - \alpha), \qquad (6)$$

where α is the degree of ionization of the acid, or base. For very weak acids and bases, α is so small, that it is negligible in comparison with $n\alpha'$ and also that $1 - \alpha$ does not differ appreciably from unity, and since α' is practically independent of the dilution and can be incorporated in the constant K, we obtain

$$n\alpha = Kv \qquad (7)$$

or

$$\alpha = \frac{Kv}{n}. \qquad (8)$$

That is, the ionization of a weak acid, or base, in the presence of one of its salts, is approximately inversely proportional to the amount of salt present.

In many of the processes of analytical chemistry, advantage is taken of the action of neutral salts on the ionization of weak acids and bases. Thus, while the concentration of hydroxyl ions in ammonium hydroxide is sufficient to precipitate magnesium hydroxide from solutions of magnesium salts, the presence of a small amount of ammonium chloride depresses the ionization of the ammonium hydroxide to such an extent that precipitation no longer takes place.

Isohydric Solutions. Arrhenius* was the first to point out what relation must exist between solutions of two electrolytes having a common ion, in order that, when mixed in any proportions, they may not exert any mutual influence. He showed that when the concentration of the common ion, in each of the two solutions, is the same before mixing, no alteration in the degree of ionization will occur after mixing. Such solutions are said to be *isohydric*. Thus, an aqueous solution containing one mol of acetic acid in 8 liters, is isohydric with an aqueous solution containing one mol of hydrochloric acid in 667 liters. On mixing these two solutions, the hydrogen ion concentration remains unchanged, and if the

* Wied. Ann., **30**, 51 (1887).

mixture is treated with a small amount of sodium hydroxide, equal amounts of sodium acetate and sodium chloride will be formed.

That isohydric solutions may be mixed without altering their respective ionizations, may be shown in the following manner:— Let C and c denote the concentrations of the undissociated portions, and let C_A, C_2, c_A, and c_2 denote the concentrations of the dissociated portions of two electrolytes, while C_2 and c_2 correspond to two different ions.

Then, we have

$$kc = c_A c_2, \tag{9}$$

and

$$KC = C_A C_2. \tag{10}$$

If V liters of the first solution be mixed with v liters of the second solution, the concentrations of the undissociated portions, and of the dissimilar ions, will be

$$\frac{CV}{V+v}, \quad \frac{cv}{V+v}, \quad \frac{C_2 V}{V+v}, \quad \text{and} \quad \frac{c_2 v}{V+v},$$

while the concentration of the common ion A, becomes

$$\frac{C_A V + c_A v}{V+v}.$$

Applying the law of mass action, we have

$$kc = \frac{C_A V + c_A v}{V+v} c_2, \tag{11}$$

and

$$KC = \frac{C_A V + c_A v}{V+v} C_2. \tag{12}$$

But equations (11) and (12) only become identical with equations (9) and (10) when $C_A = c_A$, or, in other words, no change in the degree of dissociation takes place after the two solutions are mixed.

Ionization of Strong Electrolytes. It has already been mentioned that the Ostwald dilution law, which is a direct consequence of the law of mass action, applies only to weak electrolytes. Just why the law of mass action should fail to apply to strong electrolytes is not known, but several possible causes have been suggested to account for its failure. One of the most plausible explanations is that advanced by Biltz,* who attributes its failure to hydration of the solute. If the ions become associated with

* Zeit. phys. Chem., 40, 218 (1902).

a large proportion of the solvent, the effective ionic concentration would then be, the ratio of the amount of the ion present to the amount of the *free* solvent, instead of to the *total* amount of solvent, as ordinarily calculated. This view is in harmony with certain facts which have been adduced in favor of the theory of hydration.

While the Ostwald dilution law does not apply to strongly ionized electrolytes, certain empirical expressions have been derived which hold fairly well over a wide range of dilution. Thus, Rudolphi showed that the equation,

$$\frac{\alpha^2}{(1-\alpha)\sqrt{v}} = K', \tag{13}$$

gives approximately constant values for K', with strong electrolytes. The following table gives the results obtained with solutions of silver nitrate, at 25°; the numbers in the third column were calculated by means of the Ostwald dilution law, while those in the fourth column were calculated by means of Rudolphi's dilution law.

COMPARISON OF OSTWALD & RUDOLPHI EQUATIONS

v	α	K	K'
16	0.8283	0.253	1.11
32	0.8748	0.191	1.16
64	0.8993	0.127	1.06
128	0.9262	0.122	1.07
256	0.9467	0.124	1.08
512	0.9619	0.125	1.09

The Rudolphi equation was modified by van't Hoff as follows,

$$\frac{\alpha^3}{(1-\alpha)^2 v} = K''. \tag{14}$$

This equation holds even more closely than that of Rudolphi. Of the more recent empirical equations which have been derived to express the change of conductance of an electrolyte with dilution, the equations of Kraus * and Bates † deserve special mention.

* Jour. Am. Chem. Soc., 35, 1412 (1913).

† Ibid., 37, 1421 (1915).

The equation of Kraus has the following form:

$$\left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^2 \frac{C}{\left(1-\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)} = k + k'\left(\frac{C\Lambda\eta}{\Lambda_0\eta_0}\right)^h. \qquad (15)$$

In this equation, Λ is the conductance of the electrolyte whose concentration, C, is expressed in mols per liter, η/η_0 is the ratio of the viscosity of the solution to that of the solvent, and k, k', h, and Λ_0 are empirical constants, the values of which are so chosen as to insure close agreement between the observed and calculated values of the conductance.

The equation of Bates is similar to that of the preceding equation, except that the logarithm of the left-hand side of the equation is substituted for the original expression of Kraus. The equation of Bates takes the form:

$$\log_{10}\left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^2 \frac{C}{1-\left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)} = k + k'\left(\frac{C\Lambda\eta}{\Lambda_0\eta_0}\right)^h. \qquad (16)$$

The constants, k, k', and h, are purely empirical, as in the equation of Kraus, but Λ_0 denotes the equivalent conductance at infinite dilution.

A comparison between the two equations is afforded by the following table, in which is recorded the observed and calculated values of the "corrected" equivalent conductance, $\Lambda\eta/\eta_0$, for solutions of potassium chloride, at 18°.

COMPARISON OF THE EQUATIONS OF KRAUS AND BATES

C	η/η_0	Λ (obs.)	$\Lambda\eta/\eta_0$	$\Lambda\eta/\eta_0$ (K.)	$\Lambda\eta/\eta_0$ (B.)
3	0.9954	88.3	87.89	87.4	89.3
2	0.9805	92.53	90.73	90.9	91.9
1	0.982	98.22	96.5	96.4	96.53
0.5	0.9898	102.36	101.32	101.1	101.29
0.2	0.9959	107.90	107.46	107.6	107.43
0.1	0.9982	111.97	111.77	111.9	111.73
0.05	0.9991	115.69	115.59	115.5	115.58
0.02	0.9996	119.90	119.85	119.8	119.83
0.01	0.9998	122.37	122.35	122.4	122.32
0.005	0.9999	124.34	124.33	124.4	124.38
0.002	1.0000	126.24	126.24	126.3	126.31
0.001	.....	127.27	127.27	127.2	127.32
0.0005	.....	128.04	128.04	127.6	128.05
0.0002	.....	128.70	128.70	127.9	128.68
0.0001	.....	129.00	129.00	128.1	128.96
0.0	.....	129.50	129.50	128.3	129.50

It will be observed, that for dilute solutions, the ratio, η/η_0, is practically unity, and furthermore, that the value of $C\Lambda/\Lambda_0$ is so small, that the second term on the right-hand side of both equations is negligible in comparison with the value of k.

Therefore, under these conditions, both equations reduce to the form,

$$\frac{\Lambda^2 C}{\Lambda_0 (\Lambda_0 - \Lambda)} = \text{constant}, \tag{17}$$

which will be recognized as identical with Ostwald's dilution law as given on page 502.

Heat of Ionization. The heat of ionization of an electrolyte can be calculated by means of the equation of the reaction isochore of van't Hoff (see p. 376), provided the degree of ionization at two different temperatures is known.

Since
$$K_1 = \frac{\alpha_1^2}{(1 - \alpha_1) v},$$
and
$$K_2 = \frac{\alpha_2^2}{(1 - \alpha_2) v},$$

it follows, that the heat of ionization may be calculated by means of the equation,

$$-Q = \frac{2.3026\, R \left\{ \log \frac{\alpha_2^2}{(1 - \alpha_2) v} - \log \frac{\alpha_1^2}{(1 - \alpha_1) v} \right\} T_1 T_2}{T_2 - T_1}. \tag{18}$$

Arrhenius * has shown, that this equation also applies to those electrolytes which do not obey the Ostwald dilution law. Some of the results obtained by Arrhenius are given in the following table.

It will be found that the values of the heats of ionization given in this table do not agree with the values calculated for these same substances from the data given in the table on page 358. The reason for this lack of agreement is, that the data of the earlier table refer to the heat of formation of the ions from the dissolved substance, whereas the data of the table here given, represent the combined thermal effects of solution and ionization.

* Zeit. phys. Chem., 4, 96 (1889).

HEATS OF IONIZATION OF ELECTROLYTES

Electrolyte.	Temperature.	Calories.
Acetic acid	35°	386
	21°.5	−28
Propionic acid	35°	557
	21°.5	183
Butyric acid	35°	935
	21°.5	427
Phosphoric acid	35°	2458
	21°.5	2103
Hydrochloric acid	35°	1080
Potassium chloride	35°	362
Potassium bromide	35°	425
Potassium iodide	35°	916
Sodium chloride	35°	454
Sodium hydroxide	35°	1292
Sodium acetate	35°	391

The Solubility Product. While the law of mass action does not in general, apply to the equilibrium between the dissociated and undissociated portions of an electrolyte, — except in the case of organic acids and bases, — it does apply with a fair degree of accuracy to saturated solutions of difficultly soluble salts.

A saturated solution of silver chloride affords an example of such an equilibrium. This salt is practically completely ionized in a saturated solution, as represented by the equation,

$$AgCl \rightleftarrows Ag^{\cdot} + Cl'.$$

Applying the law of mass action to this equilibrium, we obtain

$$\frac{c_{Ag^{\cdot}} \times c_{Cl'}}{c_{AgCl}} = K.$$

Since the solution is saturated, the value of c_{AgCl} must remain constant at constant temperature, and therefore,

$$c_{Ag^{\cdot}} \times c_{Cl'} = \text{constant} = s, \qquad (19)$$

where the product of the ionic concentrations, s, is called the *solubility*, or *ionic product*.

The equilibria in the above heterogeneous system may be represented thus,

$$Ag^{\cdot} + Cl' \rightleftarrows \underset{\text{(in solution)}}{AgCl} \rightleftarrows \underset{\text{(solid)}}{AgCl}.$$

The solubility product for silver chloride, at 25°, is 1.56×10^{-10}, the ionic concentrations being expressed in mols per liter. Hence,

since the two ions are present in equivalent amounts, a saturated solution of silver chloride, at 25°, must contain $\sqrt{1.56 \times 10^{-10}} = 1.25 \times 10^{-5}$ mols per liter of $Ag^{\cdot}$ and Cl' ions. In general, if the equation

$$nA \rightleftarrows n_1A_1 + n_2A_2,$$

represents the equilibrium between an electrolyte and its products of dissociation in saturated solution, we have

$$c_{A_1}^{n_1} \cdot c_{A_2}^{n_2} = s. \qquad (20)$$

The solubility product may be defined as the maximum product of the ionic concentrations of an electrolyte which can exist in equilibrium with the undissolved phase at any one temperature.

Just as the dissociation of a gaseous substance, or of an organic acid, is depressed by the addition of one of the products of dissociation, so when a substance with a common ion is added to the saturated solution of an electrolyte, the dissociation is depressed, and the undissociated substance is precipitated.

The following example will serve to illustrate how the solubility product of a substance can be determined, and how the change in solubility, due to the addition of a substance containing a common ion, may be calculated. The solubility of silver bromate, at 25°, is 0.0081 mol per liter. If we assume complete ionization, the concentration of the ions, $Ag^{\cdot}$ and BrO_3', will be identical and equal to 0.0081 mol per liter, or

$$(0.0081)\ (0.0081) = s.$$

The solubility of silver bromate in a solution of silver nitrate, containing 0.1 mol of $Ag^{\cdot}$ ions, can be calculated from the equation,

$$(0.0081)^2 = (0.0081 + 0.1 - x)\ (0.0081 - x),$$

where x represents the amount of silver bromate thrown out of solution by the addition of 0.1 mol of $Ag^{\cdot}$ ion. Since $(0.0081 - x)$ represents the concentration of BrO_3' ions, after the addition of the silver nitrate, it also represents the solubility of silver bromate under similar conditions. The effect of adding a solution of a soluble bromate, containing 0.1 mol of BrO_3' ion, will be the same as that produced by 0.1 mol of $Ag^{\cdot}$ ion.

Influence of Substitution on Ionization. Attention has already been called to the marked difference in the strength of acetic

acid produced by the replacement of the hydrogen atoms of the methyl group by chlorine. In the accompanying table the ionization constants for various substitution products of acetic acid are given.

IONIZATION CONSTANTS OF SUBSTITUTED ACETIC ACIDS

Acid.	Ionization Constant (25°).
Acetic, CH_3COOH	0.000018
Propionic, CH_3CH_2COOH	0.000013
Chloracetic, $CH_2ClCOOH$	0.00155
Bromacetic, $CH_2BrCOOH$	0.00138
Cyanacetic, $CH_2CNCOOH$	0.00370
Glycollic, $CH_2OHCOOH$	0.000152
Phenylacetic, $C_6H_5CH_2COOH$	0.000056
Amidoacetic, CH_2NH_2COOH	3.4×10^{-10}

This table affords an interesting illustration of the influence of different substituents on the strength of acetic acid. Thus, the activity of the acid is increased by the replacement of alkyl hydrogen atoms by Cl, Br, CN, OH, or C_6H_5, while the substitution of the CH_3 or NH_2 groups diminishes its activity. If we assume that the substituents retain their ion-forming capacity on entering into the molecule of acetic acid, these differences in activity can be readily explained. Thus, Cl, Br, CN, and OH tend to form negative ions, and hence increase the negative character of the group into which they enter. On the other hand, basic groups, such as NH_2, diminish the tendency of the group into which they enter to yield negative ions.

IONIZATION CONSTANTS OF PROPIONIC ACID DERIVATIVES

Acid.	Ionization Constant (25°).
Propionic acid, CH_3CH_2COOH	0.0000134
Lactic acid, $CH_3CHOHCOOH$	0.000138
β-oxypropionic acid, CH_2OHCH_2COOH	0.0000311

* Zeit. phys. Chem., 1, 105 (1887); 2, 902 (1888).

The influence of an alkyl residue on the strength of an organic acid is conditioned by its distance from the carboxyl group. This is well illustrated by the ionization constants of propionic acid and some of its derivatives. The effect of the OH group, in the α-position, is seen to be much more marked than when it occupies the β-position.

The position of a substituent in the benzene nucleus exerts a marked influence on the strength of the derivatives of benzoic acid. The ionization constants of benzoic acid, and the three chlorbenzoic acids are given in the following table.

IONIZATION CONSTANTS OF BENZOIC ACID DERIVATIVES

Acid.	Ionization Constant (25°).
Benzoic acid, C_6H_5COOH	0.000073
o-Chlorbenzoic acid, $C_6H_4ClCOOH$	0.00132
m-Chlorbenzoic acid, $C_6H_4ClCOOH$	0.000155
p-Chlorbenzoic acid, $C_6H_4ClCOOH$	0.000093

When the halogen enters the ortho-position, the strength of the acid is greatly augmented, while in the meta- and para-positions, the effect is much smaller, meta-chlorbenzoic acid being stronger than para-chlorbenzoic acid. It is a general rule, that the influence of substituents is always greatest in the ortho-position, and least in the meta- and para-positions, the order in the two latter being uncertain.

Hydrolysis. When a salt, formed by a weak acid and a strong base, such as sodium carbonate, is dissolved in water, the solution shows an alkaline reaction. On the other hand, when a salt, formed by a strong acid and a weak base, such as ferric chloride, is dissolved in water, the solution shows an acid reaction.

The process which takes place in the aqueous solution of a salt, causing it to react alkaline or acid, is termed *hydrolysis*, or *hydrolytic dissociation*. If BA represents a salt, in which B is the basic, and A is the acidic portion, then the hydrolytic equilibrium may be represented by the equation,

$$BA + H_2O \rightleftarrows BOH + HA.$$

If the base formed is insoluble, or undissociated, and the acid is dissociated, the solution will react acid. If the acid formed is insoluble, or undissociated and the base is dissociated, the solution will react alkaline. Finally, if both base and acid are insoluble, or undissociated, the salt will be completely transformed into base and acid, and, as there will be no excess of either $H^{\cdot}$, or OH' ions, the solution will remain neutral.

It is evident then, that hydrolysis is due to the removal of either one, or both, of the ions of water by the ions of the salt, to form undissociated, or insoluble substances. As fast as the ions of water are removed, the loss is made good by the dissociation of more water, until eventually, a condition of equilibrium is established. The conditions governing hydrolytic equilibrium may be determined from a knowledge of the solubility, or ionic constant of the substances involved. Thus, if the product of the concentrations of the ions, $B^{\cdot}$ and OH', exceeds that which can exist in pure water, then some undissociated, or insoluble substance will be formed. This will disturb the equilibrium of $H^{\cdot}$ and OH' ions, and a further dissociation of water will occur, until the ionic product of water is just reached. If the ions $H^{\cdot}$ and A' do not unite to form undissociated acid, the presence of an excess of $H^{\cdot}$ ions will disturb the equilibrium between pure water and its products of dissociation; or, since

$$c_{H^{\cdot}} \times c_{OH'} = K_w,$$

the concentration of OH' ions present will be $\frac{K_w}{c_{H^{\cdot}}}$, where $c_{H^{\cdot}}$ represents the total concentration of $H^{\cdot}$ ions. A similar readjustment will take place when an undissociated, or insoluble acid, and a dissociated base are formed.

We shall now proceed to consider three different types of hydrolytic dissociation, namely, (1) The hydrolysis of a salt of a strong base and a weak acid; (2) The hydrolysis of a salt of a weak base and a strong acid; and (3) The hydrolysis of a salt of a weak base and a weak acid.

(1) *Hydrolysis of a Salt of a Strong Base and a Weak Acid.* This type of reaction may be represented by the general equation

$$B^{\cdot} + A' + H_2O \rightleftarrows B^{\cdot} + OH' + HA.$$

The equilibrium constant, K_h, of this equation is

$$K_h = \frac{c_{HA} \cdot c_{OH'}}{c_{H_2O} \cdot c_{A'}}. \tag{21}$$

Since $K_w = c_{H^\cdot} \cdot c_{OH'}$ (the molecular concentration of water being regarded as constant), it follows that

$$c_{OH'} = \frac{K_w}{c_{H^\cdot}}. \qquad \text{Also} \quad K_a = \frac{c_{H^\cdot} \cdot c_{A'}}{c_{HA}}.$$

Substituting these values in equation (21), we have

$$K_h = \frac{c_{HA} \cdot K_w}{c_{H^\cdot} \cdot c_{A'}} = \frac{K_w}{K_a}. \tag{22}$$

If the degree of hydrolysis in a solution containing C gram equivalents of salt per liter be denoted by x, we may write

$$c_{HA} = xC, \quad c_{OH'} = \alpha_b xC, \text{ and } c_{A'} = \alpha_s(1 - x)C,$$

where α_b and α_s denote the degrees of dissociation of the base and salt respectively. On substituting these values in equation (22), we have

$$\frac{\alpha_b C x^2}{\alpha_s(1 - x)} = \frac{K_w}{K_a} = K_h. \tag{23}$$

Assuming that both salt and base are completely dissociated, $\alpha_b = \alpha_s = 1$, and equation (23) becomes

$$\frac{Cx^2}{(1 - x)} = \frac{K_w}{K_a} = K_h. \tag{24}$$

Since $(1 - x)$ differs but little from unity, equation (24) may take the form

$$x = \sqrt{\frac{K_w}{K_a C}}. \tag{25}$$

(2) *Hydrolysis of a Salt of a Weak Base and a Strong Acid.* The reaction is represented by the equation

$$B^\cdot + A' + H_2O \rightleftarrows H^\cdot + A' + BOH.$$

The equilibrium constant, K_h, is given by the equation

$$K_h = \frac{c_{BOH} \cdot c_{H^+}}{c_{H_2O} \cdot c_{B^+}}. \tag{26}$$

But $$c_{H^+} = \frac{K_w}{c_{OH'}}, \quad \text{and} \quad K_b = \frac{c_{B^+} \cdot c_{OH'}}{c_{BOH}}.$$

Substituting these values in equation (26), we have

$$K_h = \frac{c_{BOH} \cdot K_w}{c_{B^+} \cdot c_{OH'}} = \frac{K_w}{K_b}. \tag{27}$$

Letting α_a and α_s denote the degrees of dissociation of the acid and salt respectively, we may write

$$c_{BOH} = xC, \quad c_{H^+} = \alpha_a xC, \quad \text{and} \quad c_{B^+} = \alpha_s(1 - x)C.$$

Introducing these values into equation (27), we have

$$\frac{\alpha_a C x^2}{\alpha_s (1 - x)} = \frac{K_w}{K_b} = K_h. \tag{28}$$

If we assume that both salt and acid are completely dissociated, then $\alpha_a = \alpha_s = 1$, and equation (28) reduces to the simplified form,

$$\frac{Cx^2}{(1 - x)} = \frac{K_w}{K_b} = K_h. \tag{29}$$

(3) *Hydrolysis of a Salt of a Weak Base and a Weak Acid.* This type of reaction may be represented by the equation

$$BA + H_2O \rightleftarrows BOH + HA,$$

while the equilibrium constant is given by the equation

$$K_h = \frac{c_{BOH} \cdot c_{HA}}{c_{H_2O} \cdot c_{B^+} \cdot c_{A'}}. \tag{30}$$

But $$K_b = \frac{c_{B^+} \cdot c_{OH'}}{c_{BOH}}, \quad \text{or} \quad c_{BOH} = \frac{c_{B^+} \cdot c_{OH'}}{K_b},$$

and similarly

$$K_a = \frac{c_{H^+} \cdot c_{A'}}{c_{HA}}, \quad \text{or} \quad c_{HA} = \frac{c_{H^+} \cdot c_{A'}}{K_a}.$$

On substituting the foregoing values in equation (30), we have

$$K_h = \frac{c_{H^+} \cdot c_{OH'}}{K_a \cdot K_b} = \frac{K_w}{K_a \cdot K_b}. \tag{31}$$

Since both acid and base are only slightly dissociated, we may write $c_{HA} = c_{BOH} = xC$ and $c_{B'} = c_{A'} = \alpha_s(1 - x)C$. Assuming that the salt is completely dissociated, $\alpha_s = 1$, and on substituting the preceding values in equation (30), we have

$$K_h = \frac{x^2}{(1 - x)^2}. \tag{32}$$

On the assumption that the salt is completely dissociated, equation (31) may be written in the form,

$$x = \sqrt{\frac{K_w}{K_a K_b}}. \tag{33}$$

Salts belonging to the third type give, as a first approximation, a constant degree of hydrolysis regardless of the dilution.

As an illustration of the application of the foregoing equations, we may take the calculation of the degree of hydrolytic dissociation of potassium cyanide in 0.1 molar solution, at 25°. Potassium cyanide being a salt of a weak acid, the degree of hydrolysis can be calculated by means of equation (24),

$$\frac{Cx^2}{(1 - x)} = \frac{K_w}{K_a} = K_h.$$

Since at 25° C., $K_a = 7.2 \times 10^{-10}$ and $K_w = (1.05 \times 10^{-7})^2$, we have

$$K_h = \frac{K_w}{K_a} = \frac{(1.05 \times 10^{-7})^2}{7.2 \times 10^{-10}},$$

and

$$\frac{0.1\, x^2}{(1 - x)} = \frac{(1.05 \times 10^{-7})^2}{7.2 \times 10^{-10}},$$

hence

$$x = 0.0123.$$

Experimental Determination of Hydrolysis. In addition to the electrical conductance method outlined in the preceding chapter (p. 495), the degree of hydrolysis may also be determined by measuring the catalytic effect of the hydrogen, or hydroxyl, ion on the rate of inversion of sugar,* or on the rate of decomposition of diazoacetic ester.†

Another method, of limited applicability, to which we shall refer in the following chapter, involves the calculation of the

* Ley, Zeit. phys. Chem., 30, 222 (1899).

† Bredig and Fraenkel, Zeit. Elektrochem., 11, 525 (1905).

DEGREE OF HYDROLYSIS OF SALTS AT 25°*

Hydrolysis of Hydrochlorides of Weak Bases

(Measured by catalytic decomposition of esters)

Base	Percentage Hydrolysis	Base	Percentage Hydrolysis
Glycocoll	19	Urea	90
Asparagine	25	Acetamide	98
Acetoxime	36	Thiourea	99

Hydrolysis of Alkali Salts of Weak Acids

(Measured by catalytic saponification of esters)

Acid	Percentage Hydrolysis	Acid	Percentage Hydrolysis
Hydrocyanic	1.12	p-Chlorphenol	1.62
Acetic	0.008	p-Cyanphenol	0.29
Carbonic	3.17	p-Nitrophenol	0.16
Phenol	3.05		

Hydrolysis of Hydrochlorides of Weak Organic Bases

(Measured by rate of inversion of cane sugar)

Base	Percentage Hydrolysis	Base	Percentage Hydrolysis
Pyridine	1.2	Urea	81
Quinoline	1.2	Acetamide	78
Aniline	2.6	Asparagine	21

Hydrolysis of Metallic Chlorides

(Measured by rate of inversion of cane sugar)

Base	Percentage Hydrolysis	Base	Percentage Hydrolysis
Zinc	0.1 at 100°	Aluminium	2.7 at 77°
Lead	0.2 at 100°	Cerium	0.3 at 100°
Beryllium	1.8 at 100°	Lanthanum	0.1 at 100°
Aluminium	6.1 at 100°	Iron (ferric)	10 at 40°

Farmer, Report British Association, 240, (1901).

hydrogen ion concentration in a partially hydrolyzed solution, from measurements of electromotive force.*

The values of the degree of hydrolysis of various salts, at 25°, in 0.1 normal solutions are given in the preceding table.

The Ionization Constant of Water. One of the most accurate methods for the determination of the ionization constant of water, is based upon measurements of the degree of hydrolytic dissociation of different salts. Thus, Shields† found that a 0.1 molar solution of sodium acetate is 0.008 per cent hydrolyzed at 25°. We may consider the salt, as well as the sodium hydroxide formed from its hydrolysis, to be completely dissociated at this dilution. The ionization constant of the acetic acid formed is 0.000018, at 25°. Solving equation (24) for K_w, we have

$$K_w = K_a \cdot \frac{Cx^2}{(1 - x)}.$$

Substituting the above values in this expression, we obtain

$$K_w = 0.000018 \cdot \frac{(0.00008)^2}{(1 - 0.00008) \times 10} = 1.16 \times 10^{-14},$$

and since the ions, H· and OH′, are present in equivalent amounts we have

$$c_{H\cdot} = c_{OH'} = \sqrt{1.16 \times 10^{-14}} = 1.1 \times 10^{-7} \text{ mol per liter.}$$

Kohlrausch obtained from his measurements of the conductance of pure water, at 25°, $c_{H\cdot} = c_{OH'} = 1.05 \times 10^{-7}$ mol per liter (see p. 493).

The ionization constant of water has been measured by several other independent methods, the agreement between the results being quite satisfactory. The different methods employed may be classified as follows:

(1) Measurement of the conductance of water of a high degree of purity;

(2) Measurement of the hydrolysis of salts;

(3) Measurement of the catalytic effects of H· and OH′ on the saponification of methyl acetate;

(4) Measurement of electromotive force (see next chapter).

The following table gives a summary of the various measurements of the ionization constant of water.

* Denham, Jour. Chem. Soc., 93, 41 (1908).

† Zeit. phys. Chem., 12, 167 (1893).

IONIZATION CONSTANT OF WATER

Temperature	$c_{H^+} = c_{OH^-}$ in gram-mols per liter $\times 10^7$						
	I*	II†	III‡	IV§	V ‖	VI ¶	VII**
0°	0.298	0.37	.....	.....	.....	....	....
18	0.68	.....	0.88	.....	.....	....	....
25	0.90	1.10	1.03	1.03	1.1	1.0	1.23
50	2.1	2.96	.....	2.28	.....	....	....
75	4.1	5.3	.....	.....	.....	...	....
100	6.9	8.6	.....	.....	.....	....	....

* Noyes and Kanolt, Carnegie Inst. Publ., **63**, 346 (1907). Hydrolysis of ammonium diketotetrahydrothiazole.

† Lorenz and Bohi, Zeit. phys. Chem., **66**, 733 (1909). Electromotive force of acid-alkali cell.

‡ Kohlrausch, Wied. Ann., **53**, 209 (1894). Conductance of pure water.

§ Lundén, Jour. chim. phys., **5**, 574 (1907). Hydrolysis of ammonium borate.

‖ Shields, Zeit. phys. Chem., **12**, 167 (1893). Hydrolysis of sodium acetate.

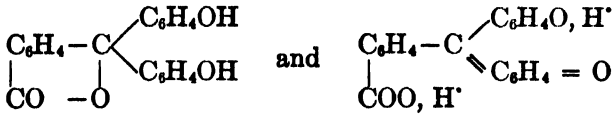
¶ Hudson, Jour. Am. Chem. Soc., **29**, 1571 (1907). Mutarotation of glucose by acids and alkalies.

** Beans & Oakes, Jour. Am. Chem. Soc., **42**, 2116 (1920). Electromotive force of cell, | Hg | HgCl,KCl | KCl | H_2O | H_2.

Theory of Indicators. When a solution of a base is titrated with an acid, the end-point is reached when the amount of acid added is just equivalent to the amount of base present. Theoretically, the solution at the end of the titration should be identical in composition with a solution prepared by dissolving a known weight of the salt formed in the process of neutralization, in the calculated amount of the solvent. Unless both acid and base have identical ionization constants, however, the salt formed will be hydrolyzed, and, therefore, the indicator should change its color when the hydrogen ion concentration of the solution acquires the same value as that which exists in a solution of the salt formed in the process of neutralization.

In order to understand the mechanism of the action of indicators, it must be remembered that indicators are, in almost all cases, weak organic acids which are capable of existing in two tautomeric forms in equilibrium with each other. For example,

phenolphthalein has been shown by Rosenstein * to exist in the two following forms:



One of these forms, which for convenience we may designate by the formula, HIn, is a non-electrolyte, while the other form, which may be represented by the formula, HIn′, is an electrolyte and, as such, is ionized in solution. The equilibria existing in a solution of such an indicator-acid may be represented in the following manner:

$$\underset{\text{(color A)}}{\text{HIn}} \rightleftarrows \underset{\text{(color B)}}{\text{HIn}'} \rightleftarrows \text{H}^{\cdot} + \text{In}'.$$

The criteria of a good indicator are, that there shall be a sharp contrast between the two colors which it exhibits in acid and alkaline media, and that the value of ratio, HIn′/HIn, shall be small. It is apparent that the addition of a strong acid to a solution containing an indicator-acid will displace the above equilibria toward the left, with the production of the so-called " acid color " of the indicator. In like manner, the addition of a base to the solution of an indicator-acid will displace the equilibria toward the right, with the development of the so-called " alkaline color " of the indicator. The " neutral color " of an indicator is intermediate between the acid and alkaline colors, and is obtained when the concentration of the hydrogen ion in the solution assumes such a value, that one-half of the indicator is in the form HIn, and the other half is in the form In′ and MIn, M being the metal of the added base.

According to the law of mass action,

$$\frac{c_{\text{H}^{\cdot}} \times c_{\text{In}'}}{c_{\text{HIn}}} = K_a, \tag{34}$$

or

$$c_{\text{H}^{\cdot}} = K_a \frac{c_{\text{HIn}}}{c_{\text{In}'}}. \tag{35}$$

If we denote by y the fraction of the indicator which exists in the form exhibiting the alkaline color, then $1 - y$ will represent the

* Jour. Am. Chem. Soc., 34, 117 (1912).

portion which is present in the form exhibiting the acid color. Therefore, equation (35) becomes

$$c_{H^+} = K_a \frac{(1 - y)}{y}. \tag{36}$$

If $y = 0.5$, the indicator will exhibit its neutral color and equation (36) will take the form,

$$c_{H^+} = K_a. \tag{37}$$

In other words, when the indicator acquires its neutral color, the indicator constant K_a, is numerically equal to the hydrogen ion concentration of the solution. The value of the fraction y, for different indicators has been determined by measuring the number of cubic centimeters of a solution of a given base which must be added to a solution containing a known amount of indicator to bring about a change of color.* Thus, it has been found that phenolphthalein changes color when $y = 0.1$. The value of the indicator constant K_a, for phenolphthalein, being 1×10^{-10}, it follows that the hydrogen ion concentration, at which the color change occurs, will be

$$c_{H^+} = 1 \times 10^{-10} \frac{(1 - 0.1)}{0.1} = 1 \times 10^{-9}.$$

Therefore, phenolphthalein will be a suitable indicator to use in titrations where the hydrogen ion concentration of the solution of the resulting salt is approximately 1×10^{-9}. For example, when acetic acid is titrated with sodium hydroxide, the proper end-point will be reached when the hydrogen ion concentration existing in the solution corresponds to that of a solution of sodium acetate of equivalent concentration. Since sodium acetate is the salt of a weak acid, it follows, that its degree of hydrolysis can be calculated by means of equation (24). Substituting the known data in this equation, we have

$$\frac{Cx^2}{(1 - x)} = \frac{1 \times 10^{-14}}{18 \times 10^{-6}},$$

it being assumed that the solution is so dilute that $\alpha_i = \alpha_b = 1$. If the concentration of the sodium acetate at the end-point is 0.1 normal, the degree of hydrolysis will be 7×10^{-5}, and the hydroxyl

* See Salm, Biochem. Zeit., 21, 131 (1909); also "Theory of Indicators," by Prideaux.

ion concentration will be 7×10^{-6}. Since $c_{H^+} \times c_{OH'} = 1 \times 10^{-14}$, it follows, that the hydrogen ion concentration in the solution will be $1 \times 10^{-14} \div 7 \times 10^{-6} = 1.4 \times 10^{-9}$. That is, the solution is actually slightly alkaline at the end-point, and consequently phenolphthalein, which undergoes a change in color at practically the same hydrogen ion concentration, is a proper indicator to employ in this titration.

REFERENCES

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A System of Physical Chemistry. Lewis. Vol. I, Chapter V.
Theory of indicators. Prideaux.
Treatise on Physical Chemistry. Taylor. Chapter XI.
Indicators. Kolthoff and Furman.

PROBLEMS

1. At 25° the specific conductance of butyric acid at a dilution of 64 liters is 1.812×10^{-4} reciprocal ohms. The equivalent conductance at infinite dilution is 380 reciprocal ohms. What is the degree of ionization and the concentration of H^+ ions in the solution? What is the ionization constant of the acid?

Ans. $\alpha = 0.0305$, $c_{H^+} = 4.765 \times 10^{-4}$ mol per liter, $K = 1.5 \times 10^{-5}$.

2. The heat of neutralization of nitric acid by sodium hydroxide is 13,680 calories, and of dichloracetic acid, 14,830 calories. When one equivalent of sodium hydroxide is added to a dilute solution containing one equivalent of nitric acid and one equivalent of dichloracetic acid, 13,960 calories are liberated. What is the ratio of the strengths of the two acids?

3. For potassium acetate we have the following data: —

v	Λ (18°)
2	67.1
10	78.4
100	87.9
10000	91.9

and $l_\infty = 64.67$, and $l_\infty = 35$. Compare the constants obtained by the
K^+ CH_3COO'
Ostwald, Rudolphi, and van't Hoff dilution laws.

4. The ionization constant of a 0.05 molar solution of acetic acid is 0.0000175 at 18°, and 0.00001624 at 52°. Calculate the heat of ionization of the acid. To what temperature does this value correspond?

Ans. 416 cal. at 35°.

5. At 20° the specific conductance of a saturated solution of silver bromide was 1.576×10^{-6} reciprocal ohms, and that of the water used was 1.519×10^{-6} reciprocal ohms. Assuming that silver bromide is completely ionized, calculate the solubility, and the solubility product of silver bromide, having given that the equivalent conductances of potassium bromide, potassium nitrate, and silver nitrate, at infinite dilution, are 137.4, 131.3, and 121 reciprocal ohms respectively.

Ans. $c_{AgBr} = 4.49 \times 10^{-7}$ mol per liter.

6. The solubility of silver cyanate, at 100°, is 0.008 mol per liter. Calculate the solubility in solution of potassium cyanate containing 0.1 mol of $K^{\cdot}$ ions.

7. Calculate the degree of hydrolytic dissociation of a 0.1 molar solution of ammonium chloride, having given the following data: — $\alpha_s = 0.86$, $\alpha_c = 0.87$, $K_{NH_4OH} = 0.000023$, and $K_w = (0.91 \times 10^{-7})^2$ at 25°.

Ans. $x = 0.006$ per cent.

8. The hydrolysis constant of aniline is 2.25×10^{-5}, and the ionization constant is 5.3×10^{-10}. Calculate the concentration of the $H^{\cdot}$ and OH' ions in water. *Ans.* $c_{H^{\cdot}} = c_{OH'} = 1.09 \times 10^{-7}$.

9. The value of the indicator constant for methyl orange is $K_a = 5 \times 10^{-4}$ and the indicator changes to its alkaline color when it is nine-tenths neutralized. Show that methyl orange is a suitable indicator to use in the titration of ammonium hydroxide with hydrochloric acid. The ionization constant of ammonium hydroxide may be assumed to be 18×10^{-6}.

10. The value of the indicator constant for rosolic acid is $K_a = 4 \times 10^{-8}$ and the indicator changes to its alkaline color when it is one-tenth neutralized. Would this be a suitable indicator to use in the preceding titration?

CHAPTER XVII

ELECTROMOTIVE FORCE

Galvanic Cells. Since the year 1800, when Volta invented his electric pile, many different forms of galvanic cells have been introduced. It is not our purpose to give a detailed account of these cells, but rather to give a brief outline of the theories which have been advanced in explanation of the electromotive force developed in such cells. When two metallic electrodes are immersed in a solution of an electrolyte, a current will flow through a wire connecting the electrodes, provided the two metals are dissimilar. Not only can an electric current be obtained from a combination of two different metals in the same electrolyte, but also from two different metals in two different electrolytes, from the same metal in different electrolytes, or from the same metal in two different concentrations of the same electrolyte. In order that the electromotive force of the combination shall remain constant, it is necessary that the chemical changes involved in the production of the current shall neither destroy the difference between the electrodes, nor deposit upon either of them a non-conducting substance. A galvanic combination which fulfils these conditions very satisfactorily is the Daniell cell. This cell consists of zinc and copper electrodes immersed in solutions of their salts, as represented by the scheme,*

$$\bar{Zn} - \text{Sol. of } ZnSO_4 \;||\; \text{Sol. of } CuSO_4 - \dot{Cu},$$

in which the two vertical lines indicate a porous partition separating the two solutions. When the zinc and copper electrodes are connected by a wire, a current of positive electricity passes, from the copper to the zinc, along the wire. Zinc dissolves from the zinc electrode, an equivalent amount of copper being displaced from the solution and deposited simultaneously on the copper electrode.

* The order of arrangement of all cells discussed in this chapter will be such that the positive terminal is at the right of the galvanic chain with an arrow beneath pointing toward the positive pole.

The result of these two processes is summarized by the equation

$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

Since only the distribution and not the amount of SO_4'' ions undergoes change, the cell reaction may be expressed in the ionic form by the equation,

$$Zn + Cu^{\cdot\cdot} = Cu + Zn^{\cdot\cdot}.$$

In terms of the electron theory, the two electrode processes in the Daniell cell may be written in the following manner:

(1) Anode reaction, $Zn = Zn^{\cdot\cdot} + 2\ominus$;

(2) Cathode reaction, $Cu^{\cdot\cdot} + 2\ominus = Cu$.

In the anode reaction, for each zinc ion formed, two electrons are set free, whereas in the cathode reaction, for each copper ion discharged, two electrons are discharged. The net result of these two reactions is the transfer of two electrons from the copper through the solution to the zinc. In other words, the direction of flow of the electron stream is opposite to the direction of flow of the current.

As long as only a moderate current flows through the cell, the original nature of the electrodes is not modified, the only change which occurs being the gradual dilution of the copper sulphate, owing to the separation of copper and its replacement by zinc. If the loss of copper sulphate is replaced, the electromotive force of the cell will remain constant. If, after the cell is assembled, the circuit remains open, the copper sulphate will slowly diffuse into the solution of zinc sulphate, and metallic copper will ultimately be deposited on the zinc electrode. In this way miniature, local galvanic cells will be formed on the surface of the zinc, and the metal will dissolve as though the main circuit were closed. Until this deposition takes place, the cell may be left on open circuit without danger of deterioration. Unless chemically pure zinc is used, local action is likely to occur, owing to the formation of local galvanic couples between the impurities in the electrode — chiefly iron — and the zinc. This action may be prevented by amalgamating the zinc electrode. In this process the mercury dissolves the zinc and not the iron, a uniform surface of the former metal being produced.

An interesting experiment, due to Ostwald,* illustrates the con-

* Phil. Mag. [5], 32, 145 (1891).

ditions essential to the continuous production of an electric current. Two electrodes, one of amalgamated zinc and the other of platinum, are each immersed in a solution of potassium sulphate, the two solutions being separated by a porous cup. When the two electrodes are connected by means of a wire, no permanent flow of current occurs. An inappreciable quantity of zinc, however, goes into solution, since any current must necessarily first liberate potassium at the platinum electrode. The potassium thus set free reacts with the water. This process requires the expenditure of more energy than the solution of the zinc supplies. If sulphuric acid is added to the compartment containing the zinc, the condition of the system will be unchanged; i.e., the zinc will remain undissolved. If, on the other hand, a few drops of sulphuric acid are added to the compartment containing the platinum electrode, bubbles of hydrogen will appear, and the zinc will dissolve with the simultaneous development of an electric current. This experiment shows, that in order that positively charged ions may enter a solution, an equivalent amount of negatively charged ions must be introduced, or an equivalent amount of positively charged ions must be removed.

Reversible Cells. Galvanic cells are either *reversible*, or *irreversible*, according as the processes taking place within them can be reversed or not. If we disregard the slow processes of diffusion, the Daniell cell may be taken as an example of an almost perfect reversible element. If an electromotive force slightly less than that of the cell be applied to it, in the reverse direction, the current within the cell will flow from the zinc to the copper electrode, as usual. On the other hand, if the external electromotive force slightly exceeds that of the cell, the current within the cell will flow in the reverse direction, zinc being deposited and copper dissolved. Any cell from which gas is evolved is irreversible, since the passage of a current in the reverse direction cannot restore the cell to its original condition.

Relation between Chemical Energy and Electrical Energy. Helmholtz and Thomson were the first to propose a satisfactory theory of the action of the reversible cell. According to this theory, the energy of the chemical process taking place within the cell was considered to be completely transformed into electrical energy. It was soon shown that this theory is inadequate, since, with the exception of the Daniell cell and a few other cells, the

chemical energy is not equivalent to the electrical energy produced.

The exact quantitative relationship between the chemical energy transformed, and the maximum electrical energy developed, by a reversible galvanic cell can readily be derived by means of the familiar Gibbs-Helmholtz equation (see p. 184),

$$W + U = T\left(\frac{dW}{dT}\right), \tag{1}$$

where W denotes the maximum work obtainable from a completely reversible, isothermal process, and where U is the increase in the total energy of the system. If the maximum work be expressed in terms of electrical energy, we will have

$$W = nFE, \tag{2}$$

in which F is the faraday, E, the electromotive force of the cell and n, the number of unit charges transferred. On differentiating equation (2), we obtain

$$dW = nFdE, \tag{3}$$

and on substituting these values of A and dW in equation (1) we have

$$nFE + U = nFT\left(\frac{dE}{dT}\right),$$

or

$$E \quad \frac{-U}{nF} + T\left(\frac{dE}{dT}\right). \tag{4}$$

Since the decrease in internal energy is equal to the heat evolved at constant volume, equation (4) may be written in the form,

$$E = \frac{-Q_v}{nF} + T\left(\frac{dE}{dT}\right). \tag{5}$$

This equation expresses the electromotive force of a reversible cell in terms of the temperature coefficient of the cell, and the heat of the chemical reaction occurring within the cell. Equation (5) may be employed to calculate the heat of the cell reaction; thus, the electromotive force of the Daniell cell, at 15° C., is $E = 1.09337$ volts while the temperature coefficient, $dE/dT = 0.000429$ volt per degree. On substituting these values in equation (5), we have

$$Q = \frac{-2 \times 96{,}500}{4.182}(1.09337 + 288 \times 0.000429),$$

$$= -56{,}160 \text{ calories.}$$

The heat of the cell reaction as determined by direct experiment is −55,189 calories.

In the following table, compiled by Jahn,* the values of the heat of the reaction of several different cells are given, (a) as calculated by the Gibbs-Helmholtz equation, and (b) as calculated by the Helmholtz-Thomson rule.

EXPERIMENTAL VERIFICATION OF GIBBS-HELMHOLTZ EQUATION

Cell	E	dE/dT	U (calc.)	U (obs.)	nFE/J
$Cu\|Cu(C_2H_3O_2)_2$ solution $\|Pb(C_2H_3O_2)_2$, 100 $H_2O\|Pb$ (0°)	0.4764	+0.000385	16,900	17,533	21,684
$Ag\|AgCl, ZnCl_2$, 100 $H_2O\|Zn$ (0°)	1.015	−0.000402	51,989	52,046	46,907
$Hg\|HgO$ n NaOH$\|H_2$ (18°)	0.9243	−0.00031	46,750	46,700	42,590
$Hg\|HgCl$ 0.01 n KCl‖ n $KNO_3\|0.01$ n-KOH$\|Hg_2O\|Hg$ (18.5°)	0.1656	+0.000387	−3,710	−3,280	7,566

It will be seen that the agreement between the observed and calculated values of U is as close as could be expected, whereas, the figures given in the last column, calculated according to the Helmholtz-Thomson rule, differ widely from the experimentally determined values. When $\frac{dE}{dT} = 0$, E becomes equal to $\frac{-Q_v}{nF}$; in other words, when the temperature coefficient of the cell is zero, the electrical energy is equal to the chemical energy. This is approximately true of the Daniell cell, which has an extremely small temperature coefficient.

For cells in which the electromotive force varies appreciably with the temperature, it is possible to calculate the value of the electromotive force at any temperature by means of the Gibbs-

* Wied. Ann., 28, 21 (1886).

Helmholtz equation, provided the temperature coefficient is known. The Gibbs-Helmholtz equation shows that the amount of heat accompanying a chemical process does not alone furnish a measure of the electrical energy which may be obtained from it, since the heat which is absorbed from the surrounding medium may also be transformed into electrical energy, or the output of electrical energy may be less than the heat of the reaction within the cell.

Heat of Ionization. If the difference of potential between a metal and the solution of one of its salts is known, it is possible to calculate the heat of ionization of the metal by means of the Gibbs-Helmholtz equation,

$$E = \frac{-Q_v}{nF} + T\frac{dE}{dT},$$

provided the variation of the electromotive force with temperature is known. Solving the equation for Q_v, the heat evolved when one mol of ions is formed at the electrode, we have

$$-Q_v = \left(E - T\frac{dE}{dT}\right)nF.$$

For example, the potential of zinc against a molar solution of zinc chloride is -0.497 volt, at 25°, and the temperature coefficient of electromotive force is 0.000664 volt per degree. Substituting in the equation, we have

$-Q_v = [-0.497 - (273 + 25) \times 0.000664] (2 \times 96{,}540 \times 0.2394)$
or $Q_v = 32{,}120$ calories.

That is, the heat of the reaction,

$$Zn + 2\,(+) \rightarrow Zn^{\cdot\cdot},$$

is $-32{,}120$ calories per mol of zinc.

Solution Pressure. It is a familiar fact, that water has a tendency to assume the form of vapor, and if the vapor be continually removed from its surface, a definite mass of water will gradually be completely transformed into the state of vapor. The pressure of the vapor, at any one temperature, is a measure of the tendency of water to undergo this transformation. This tendency of water to assume a form other than that in which it actually exists, is typical of all substances. Attention has already been

directed to this fact in connection with the application of the law of mass action to heterogeneous equilibria. It was then pointed out, that all solids have a definite vapor pressure at a definite temperature, which is independent of the amount of solid present. When a solid, such as cane sugar, is brought in contact with water, it tends to pass into solution. This tendency is constant, at constant temperature, since the active mass of the solid is constant. From the close analogy between the vapor state and the dissolved state, the tendency of a solid to pass into solution is termed the *solution pressure.* A dissolved solid, on the other hand, also shows a tendency to separate from the solution as the concentration is increased. When the solution becomes supersaturated, the tendency of the solute to separate in the solid form is greater than the tendency of the solid to dissolve. It is evident, from these considerations, that the pressure exerted by the dissolved solid is its osmotic pressure, and whether the solid will dissolve, or separate from the solution depends upon whether the solution pressure is greater, or less than the osmotic pressure.

This conception of solution pressure was introduced by Nernst,* and in conjunction with the theory of electrolytic dissociation, it has proved of great value in affording a much deeper insight into the mechanism of the development of differences of potential within a galvanic cell. Thus, when a metal is dipped into water it tends to dissolve, owing to its solution pressure, P, and, in consequence of this tendency, it sends a certain number of positive ions into solution. The solution thus becomes positively charged, and the metal, which was initially neutral, acquires a negative charge, due to the loss of a certain amount of positive electricity. This process will cease when the solution becomes so strongly charged with positive electricity that it prevents the separation of any more positive ions from the metal. Relatively few ions leave the metal before equilibrium is established, since the charge on each ion is so great; in fact, the concentration of metal ions in the solution is much too small to be detected analytically. When a metal is dipped into a solution of one of its salts, however, the conditions are altered. In this case, the positive ions of the metal, already present in the solution, oppose the entrance of more positive ions, and the equilibrium between these two opposing tendencies will be conditioned by the relative values of the solution

* Zeit. phys. Chem., 4, 150 (1889).

pressure, P, of the metal, and the osmotic pressure, p, of the ions of the dissolved salt.

It is evident that the three following conditions are possible:

(1) If $P > p$, the metal will continue to send ions into the solution until the accumulated charges in the solution oppose further action. The solution acquires a positive charge, and the metal a negative charge.

(2) If $P < p$, the positive ions of the dissolved salt will separate on the metal until the accumulated charges oppose further action. The metal acquires a positive charge and the solution a negative charge.

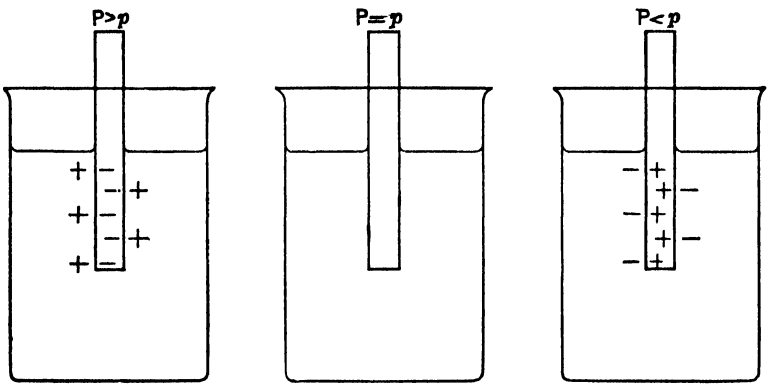


Fig. 139

(3) If $P = p$, no action will take place and no difference of potential will be established between the metal and the solution. These three cases are represented diagrammatically in Fig. 139. When equilibrium is established and the metal is negative against the solution, the metal is surrounded by a layer of positively charged ions. This constitutes what is known as a Helmholtz *electrical double layer*. If positive electricity be communicated to the metal, the double layer will be broken, and more ions will pass from the metal into the solution, but as soon as the supply of positive electricity is cut off, the double layer will again be formed. Similarly, when the metal is positive against the solution, an electrical double layer will be formed, the metal being surrounded by a layer of negatively charged ions.

The actual existence of a Helmholtz double layer has been demonstrated by Palmaer.* In his experiments, Palmaer allowed exceedingly minute globules of mercury to fall into a dilute solution of mercurous nitrate, contained in a tall vessel, the bottom of which was covered with a layer of pure mercury, as shown in Fig. 140. Since the solution pressure of mercury is less than the osmotic pressure of the $Hg^{\cdot}$ ions, each drop of mercury, as it enters the solution, will acquire a positive charge, and if the theory of the electrical double layer is correct, this positively charged globule should attract negatively charged ions and drag them down through the solution. When the globule reaches the mercury, at the bottom of the vessel, it will give up its positive charge, and as many $Hg^{\cdot}$ ions will pass into solution as there are NO_3' ions in the double layer. The solution will thus become more concentrated just above the layer of mercury on the bottom of the vessel. Palmaer's experiments showed that this difference in concentration is actually produced, in some cases the concentration in the upper part of the solution being reduced as much as 50 per cent.

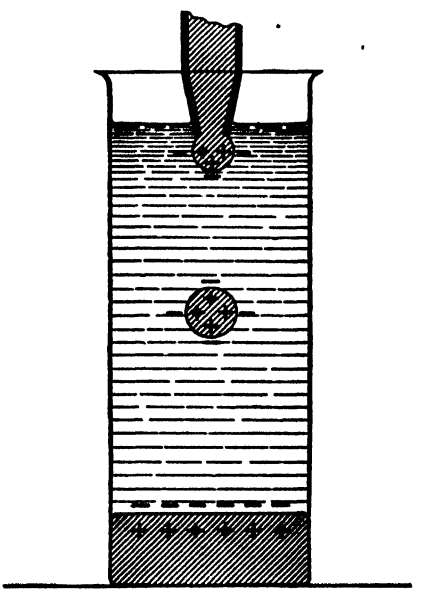


Fig. 140

The metals sodium, potassium, zinc, cadmium, cobalt, nickel, and iron are negative against solutions of their salts; i.e., $P > p$. The noble metals are generally positive against solutions of their salts, or $P < p$. The elements which form anions are, so far as is known, positive to solutions of their salts. Electrolytic solution pressure varies with the temperature, with the nature of the solvent, and also with the concentration of the active substance in the electrode.

The Difference of Potential between a Metal and a Solution. From the foregoing considerations, it is possible to derive an

* Zeit. phys. Chem., **25**, 265 (1898); **28**, 257 (1899); **36**, 664 (1901).

equation expressing the difference of potential between a metallic electrode and a solution of one of its salts.

Let us imagine one gram-ion of a metal to be transferred from the electrolytic solution pressure P, to the osmotic pressure p. The osmotic work done will be

$$\int v\,dp = RT\int\frac{dp}{p}. \tag{6}$$

Integrating this expression, we have

$$\text{Osmotic work} = RT\ln p + i, \tag{7}$$

where i is the constant of integration. The corresponding electrical energy gained is nFE, where E is the difference of potential between the metal and the solution, $F = 1$ faraday $= 96{,}500$ coulombs, and n is the valence of the metal. Since the osmotic work done is equivalent to the electrical energy gained, we may equate these two expressions, as follows:

$$nFE = RT\ln p + i.$$

Since $E = 0$ when $P = p$, the integration constant, i, in the above equation is equal to $-RT\ln P$. Therefore $nFE = RT\ln p - RT\ln P$,

or

$$E = \frac{RT}{nF}\ln\frac{p}{P}. \tag{8}$$

Expressing both sides of equation (8) in electrical units, and transforming to Briggsian logarithms, we obtain

$$E = \frac{2\times 4.182}{96{,}500\times n\times 0.4343}T\log\frac{p}{P},$$

or

$$E = \frac{0.0002}{n}T\log\frac{p}{P}. \tag{9}$$

For univalent ions at 17°, we have

$$E = 0.0575\log\frac{p}{P}. \tag{10}$$

In a galvanic cell composed of two metals, each immersed in a solution of one of its salts, a difference of potential may be established (1) at the junction of two metals, (2) at the junction of

the two solutions, and (3) at the points of contact of the metals with their respective solutions. If the temperature remains constant, (1) is negligible, and in general, (2) is exceedingly small; therefore, the electromotive force of the cell may be considered as due to the differences of potential arising at the two electrodes. Assuming the temperature to be 17°, the electromotive force of the cell will be

$$E = E^+ - E^- = \frac{0.0575}{n} \log \frac{p_2}{P_2} - \frac{0.0575}{n} \log \frac{p_1}{P_1}, \qquad (11)$$

where E^+ = single electrode potential of positive pole of cell and where E^- = single electrode potential of negative pole of cell.

The Measurement of Electromotive Force. The value of the electromotive force of a cell may vary with the conditions of measurement. Since, according to Ohm's law, $E = I\ (R + r)$, where R is the resistance of the external circuit, and r is the internal resistance of the cell, it follows that the fall of potential, IR, in the external circuit will only be equal to E, when r is negligible in comparison with R. Furthermore, when the circuit is closed, the electrodes of the cell frequently become polarized, owing to the deposition of the products of electrolysis, and an opposing electromotive force is set up

To avoid these difficulties, the electromotive force is usually measured on open circuit by the Poggendorff compensation method. In this method, the electromotive force to be measured is just balanced by an equal and opposite electromotive force, so that no current passes. The arrangement of the apparatus for such measurements is shown in Fig. 141. If the two ends of the wire, AB, of a Wheatstone bridge are connected to a lead accumulator, C, there will be a uniform fall of potential along its entire length. The amount of fall, along any portion AD, will be proportional to the length AD, and equal to the fraction $\frac{AD}{AB}$ of the total fall of potential along the entire length of the wire. Now let one terminal of a cell, whose electromotive force is less than that of C, be connected to A, and the other terminal be connected, through a galvanometer G, with a sliding contact D, the two cells, E and C, working in opposition. A current will flow through the circuit $AEGD$, and will be indicated by the galvanometer at all positions, except that at which the fall of potential along the wire,

from A to D, is equal to the electromotive force of E. Hence we have

$$\text{e.m.f. of } C : \text{e.m.f. of } E :: AB : AD,$$

from which the value of the electromotive force of the cell E, can be calculated. Since the electromotive force of a lead accumulator is not quite constant, it is customary, after having deter-

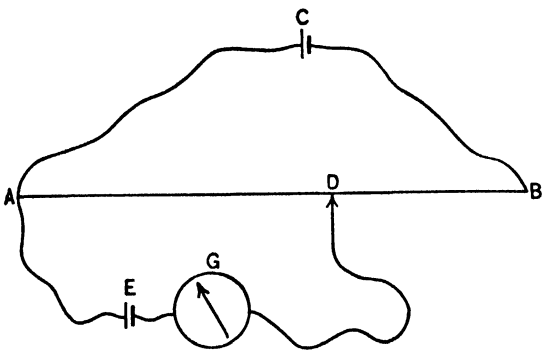


Fig. 141

mined the point D, to substitute a standard cell for E, and balance this against the accumulator, finding a new point of balance, D'. We now have the proportion,

$$\text{e.m.f. of } C : \text{e.m.f. of standard} :: AB : AD'.$$

Combining these two proportions, we obtain

$$\text{e.m.f. of } E : \text{e.m.f. of standard} :: AD : AD'.$$

Instead of using a galvanometer, as a "null" instrument for indicating when the point of balance has been reached, a capillary electrometer may be employed.

In precise determinations of electromotive force, the simple slidewire bridge and capillary electrometer is usually replaced by a potentiometer and sensitive galvanometer, thereby greatly increasing the accuracy of the measurements. Recently, Beans and Oakes* have developed a method, whereby the electromotive force of cells having very high internal resistance can be measured with an accuracy of 0.5 millivolt. In this method, the cell is connected to a condenser of suitable capacity, and when a suffi-

* Jour. Am. Chem. Soc., 42, 2116 (1920).

cient quantity of electricity has accumulated, the condenser is discharged through a calibrated ballistic galvanometer. In addition to its accuracy, this method involves the use of much less expensive apparatus than is required in the more elaborate potentiometric methods.

Standard Cells. It is apparent that the accuracy of all measurements of electromotive force is dependent upon the cell employed as a standard. Much time has been devoted to the study of various reversible elements, with a view to establishing a standard of electromotive force. As a result, we have the complete specifications for two standard cells, either of which may be readily reproduced.

(a) *The Weston, or Cadmium Standard Cell.* The most widely used standard of electromotive force is the so-called Weston cell, made up according to the scheme,

$$\text{Cd} - \text{Solution } CdSO_4 \,||\, \text{Solution } Hg_2SO_4 - \text{Hg}.$$

A short platinum wire is sealed through the bottom of each limb of an H-shaped vessel. In one limb is placed a small amount of a 10 to 15 per cent cadmium amalgam, together with a layer of small crystals of $CdSO_4 \cdot \frac{8}{3} H_2O$. In the other limb is placed a small amount of pure mercury, over which is a layer of a paste, composed of solid mercurous sulphate and a saturated solution of cadmium sulphate. The cell is then filled with crystals of cadmium sulphate and a saturated solution of cadmium sulphate, after which the two limbs of the cell are hermetically sealed. If carefully prepared, this cell will remain unaltered for years and will have an electromotive force, at 20°, of 1.0183 volts. In addition to the fact that it can be so easily reproduced, the temperature coefficient of the cell is almost negligible.

The electromotive force of a Weston standard cell at any temperature t, is given by the formula,

$$\text{e.m.f. at } t^\circ = 1.0183 - 0.000038\,(t - 20). \qquad (12)$$

(b) *The Clark, or Zinc Standard Cell.* Until several years ago, the Clark cell was considered to be the most trustworthy standard of electromotive force. This cell is made up according to the scheme,

$$\text{Zn} - \text{Solution } ZnSO_4 \,||\, \text{Solution } Hg_2SO_4 - \text{Hg}.$$

The construction of the cell is similar to that of the Weston cell. It may be reproduced with as great accuracy and with no more trouble than the Weston cell, but its relatively large temperature coefficient renders it less satisfactory. The electromotive force of the Clark standard cell at any temperature t, may be calculated by means of the formula,

$$\text{e.m.f. at } t^\circ = 1.4328 - 0.00119\,(t - 15) - 0.00007\,(t - 15)^2. \quad (13)$$

The Capillary Electrometer. In 1873, Lippmann* showed that when a globule of mercury is negatively electrified its surface tension increases and the drop shrinks. If sufficient negative electricity is imparted to the mercury it is possible to restore the globule to its original form. On applying more negative electricity, the globule of mercury again expands. Lippmann concluded from his experiments, that the difference of potential arises at the surface of contact between the mercury and the solution of the electrolyte, and that the surface tension of the mercury is a function of the difference of potential. Making use of this principle, he constructed the capillary electrometer, a convenient form of which is shown in Fig. 142. The bulb A, through the bottom of which a platinum wire is sealed, contains pure mercury and dilute sulphuric acid (1 : 6). Pure mercury is poured into the other limb of the electrometer until it stands at B in the wide tube, and at C in the capillary tube. Owing to the capillary depression of the mercury, C lies below B. Electrical connection with the mercury is established at B, by means of a platinum wire. The position of the mercury in the capillary is determined by its surface tension; if the surface tension is increased, the mercury will descend; if it is diminished, the mercury will ascend. If a negative charge is communicated to the mercury at B, the surface tension will be increased and the meniscus will descend; if a positive charge is imparted to the mercury at B, the surface ten-

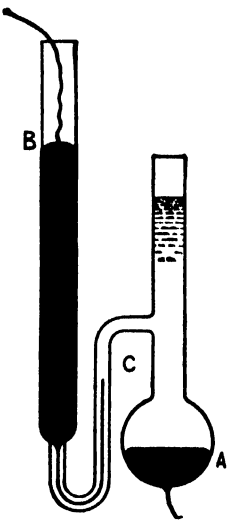


Fig. 142

* Pogg. Ann., 149, 546 (1873).

sion will be diminished and the meniscus will ascend. The amplitude of the movement of the meniscus is an inverse function of the diameter of the capillary tube. If the meniscus be observed through a microscope provided with an eye-piece micrometer, as shown in Fig. 143, it is possible to detect very slight movements, and to measure differences of potential less than 0.0001 volt. The capillary electrometer is an excellent "null" instrument.

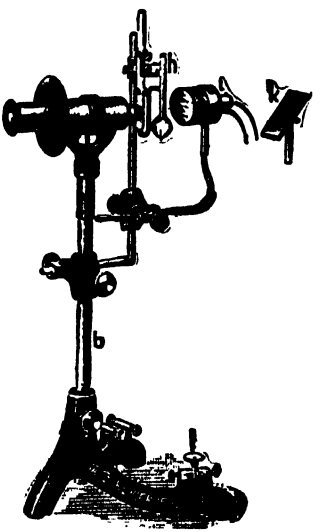


Fig. 143

The Potentiometer. The capillary electrometer and simple slide-wire bridge have been almost entirely superseded by the galvanometer and potentiometer. The latter, as its name implies, is an instrument for measuring differences of potential. The underlying principle involved in the construction of all types of potentiometer is the total, or partial, balancing of the unknown difference of potential against a variable difference of potential, the value of the latter being determined by reference to a standard of electromotive force, such as the Weston cell.

In order to measure smaller differences of potential than is possible with the slide-wire bridge — which is the simplest form of potentiometer — an accurately determined electromotive force is generally balanced across a known resistance included in the potentiometer circuit. Since the current is the same throughout this circuit, the fall of potential per unit of resistance becomes known as soon as a balance is secured.

The potentiometer of Leeds and Northrup is especially adapted to meet the requirements of the physical chemist for the precise and rapid measurement of electromotive force. A diagram of the electrical connections of this instrument is given in Fig. 144.

The battery, *W*, acts as the source of current in the circuit *OAMDB*; in this circuit is a series of fifteen five-ohm coils, *AD*, accurately adjusted to equality. In series with these coils is a five-ohm slide-wire, *DB*, wound on a marble cylinder. A

standard cell is connected from the point 0.5 to the switch T, the latter being turned to the point on the accompanying dial which corresponds to the certified voltage of the standard cell. The rheostat, R, is adjusted until the galvanometer — which can be included in the circuit with the standard cell by throwing the switch, U — gives no deflection. The current which then flows

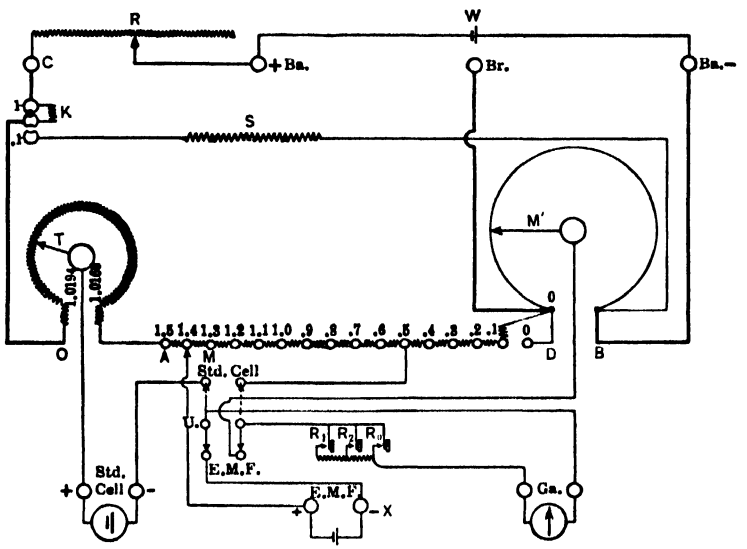


Fig. 144

through the potentiometer circuit will be precisely one-fiftieth of an ampere. The switch, U, is now turned so as to connect the unknown electromotive force, X, through the galvanometer to the moving contact, M, and the sliding contact, M'. The two contact points, M and M', are then adjusted until the galvanometer indicates that no current is flowing through the circuit. The value of the unknown electromotive force may then be read from the settings of M and M'. The former of these reads to tenths of a volt and the latter, by estimating fractions of the smallest division, to hundred-thousandths of a volt. By changing the plug at K from the position marked 1 to that marked 0.1, the sensitivity of the instrument can be increased ten-fold, thereby enabling the experimenter to read to millionths of a volt.

Reference Electrodes. The method commonly employed for the measurement of the difference of potential between a metal and a solution, is based upon the use of an electrode in which the difference of potential between the electrode and a certain solution of one of its salts is known. Such an electrode is called a *reference electrode.* If a cell is made up by combining the reference electrode with the electrode whose potential is to be determined, it is possible, from measurements of the resulting electromotive force, to calculate the value of the unknown difference of potential. The most convenient electrode to prepare, is the normal calomel electrode, a satisfactory form of which is shown in Fig. 145. The bottom of the electrode vessel is covered with a layer of pure mercury, upon which is poured a paste, prepared by rubbing together in a mortar mercury and calomel, moistened with a molar solution of potassium chloride. The vessel is then filled with a molar solution of the same salt which has been saturated with calomel by prolonged shaking with the latter. Connection with the mercury is established by means of a platinum wire sealed into a glass tube A, the latter being passed through the rubber stopper which closes the vessel. In using the calomel electrode, the bent side tube, C, is filled with molar potassium chloride by applying suction at the side tube B, which is then closed by means of a pinch-cock.

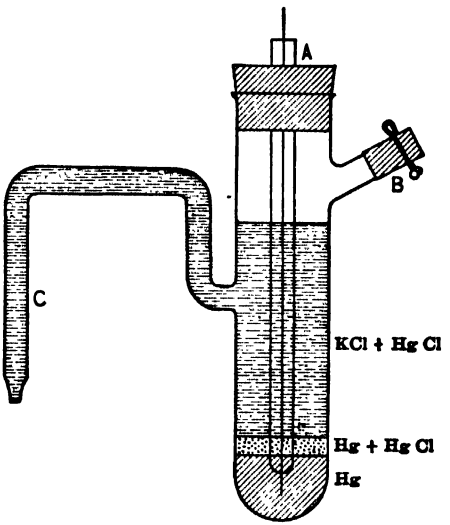


Fig. 145

The difference of potential, at any temperature t, of the calomel electrode prepared as described, and represented by the scheme,

$$\text{Hg} - \text{Solution HgCl in molar KCl,}$$

is $$E = +0.56\ \{1 + 0.0006\ (t - 18)\}\ \text{volt.} \qquad (14)$$

The positive sign before the value 0.56, indicates that the electrode is positive to the solution. In order to measure the potential of another electrode by means of the calomel electrode, the arrangement shown in Fig. 146 is commonly used. Here, *A* represents the "half-element" of which the potential is to be determined, *B* represents the side tube of the calomel electrode, and *C* represents an intermediate connecting vessel containing a molar solution of potassium chloride. In cases where potassium chloride forms a precipitate with the electrolyte in *A*, the solution in *C* may be replaced by a molar solution of potassium nitrate, without altering the value of the electromotive force of the cell.

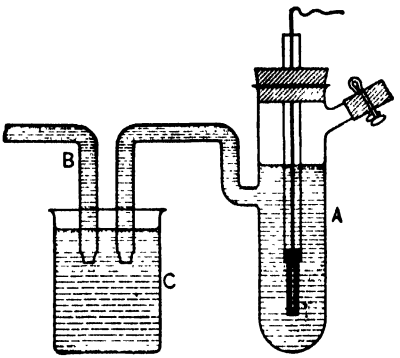


Fig. 146

The original measurement of the potential of the calomel electrode was made by forming a cell with this and another electrode whose potential against its solution is zero. Such an electrode is known as a *null electrode*. Thus, if a copper electrode is immersed in a solution of copper sulphate, the $Cu^{\cdot\cdot}$ ions will leave the solution and charge the electrode positively. If now a solution of potassium cyanide is added, the nearly undissociated salt, $K_2Cu_2(CN)_4$, will be formed, and by adding a sufficient amount of the solution, the concentration of the $Cu^{\cdot\cdot}$ ions may be reduced until the metal and the solution have the same potential. The addition of more potassium cyanide will still further diminish the osmotic pressure of the $Cu^{\cdot\cdot}$ ions, and the electrode will acquire a negative charge. Similarly, mercury in a solution of a double cyanide may be used as a null electrode.

Another form of null electrode is the so-called *dropping electrode* of Helmholtz.* The principle involved in this electrode has already been discussed in connection with Palmaer's experiment (p. 535). An extremely fine stream of mercury is allowed to flow from a funnel having a minute capillary orifice, the stem of the funnel dipping below the surface of a molar solution of potassium chloride containing mercurous ions. As each little globule

* Ann. der Phys., 44, 42 (1890)

enters the solution, it acquires a positive charge and attracts the negatively charged ions of the electrolyte, dragging them down with itself. When each globule reaches the layer of mercury at the bottom of the vessel, its surface and capacity are diminished, and as many $Hg^{\cdot}$ ions leave the layer of mercury and enter the solution as there were negatively charged ions carried down by the globule. This process continues until the osmotic pressure of the remaining ions is equal to the solution pressure of the metal. The mercury, both in the stream and at the bottom of the vessel, has the same potential as the solution. If now, the difference of potential between the mercury in the funnel and the mercury in the vessel be measured, we shall obtain the potential of mercury against a molar solution of potassium chloride, containing mercurous ions.

The dropping electrode was for a long time regarded as an ideal standard of potential, but a number of serious objections to it have been pointed out. Until a wholly satisfactory standard of potential is obtained, it has been proposed that the potential of the *hydrogen electrode* be adopted as the standard. This consists of a strip of platinized platinum, half being immersed in pure hydrogen gas, and half in a solution of sulphuric acid of such concentration that it shall contain 1 gram of hydrogen ions per liter. The use of the hydrogen electrode as a standard is purely arbitrary, but there are many advantages in referring differences of potential to this standard. Owing to certain experimental difficulties attending the use of this electrode, it is customary to make the actual measurements with the calomel electrode, and then refer them to the hydrogen standard, taking the potential of the calomel electrode as +0.283 volt, when referred to the hydrogen electrode as zero. *The positive sign indicates that the electrode is positive towards the normal hydrogen electrode.*

Measurement of the Difference of Potential between a Metal and a Solution. The difference of potential between a metal and a solution of one of its salts is easily determined by means of the calomel electrode. For example, in order to determine the potential of zinc against a molar solution of zinc sulphate, the electromotive force E, of the combination,

$$Zn - ZnSO_4 \,||\, m\ KCl,\ Hg_2Cl_2 - Hg,$$
(cal. electrode)

is measured, and found to be 1.08 volts, the mercury being the positive terminal of the cell. Applying the Nernst equation,

$$E = E^+ - E^- = \frac{RT}{nF}\ln\frac{p_2}{P_2} - \frac{RT}{nF}\ln\frac{p_1}{P_1}, \qquad (15)$$

in which P_1 and p_1 denote the solution pressure and the osmotic pressure of the zinc ions, and P_2 and p_2 denote the solution pressure and the osmotic pressure of the mercury ions, we have

$$1.08 = 0.283 - \frac{RT}{2F}\ln\frac{p_1}{P_1},$$

or

$$\frac{RT}{2F}\ln\frac{p_1}{P_1} = 0.283 - 1.08 = -0.797 \text{ volt},$$

referred to the normal hydrogen electrode as zero. That is, the zinc electrode is negative against a molar solution of zinc sulphate, the difference of potential being -0.797 volt. As an example of a cell in which the mercury of the calomel electrode is the negative terminal of the cell, we may take the following combination: —

$$\text{Hg} - \text{Hg}_2\text{Cl}_2, \text{m KCl} \,||\, \text{m CuSO}_4 - \text{Cu}.$$

The electromotive force of this cell is 0.025 volt. Since the positive current flows from the copper to the mercury outside, we have

$$E = 0.025 = \frac{RT}{2F}\ln\frac{p_1}{P_1} - 0.283,$$

or

$$\frac{RT}{2F}\ln\frac{p_1}{P_1} = 0.025 + 0.283 = 0.308 \text{ volt},$$

referred to the normal hydrogen electrode as zero. That is, the copper electrode is positive against a molar solution of copper sulphate. From the above results, it is possible to calculate the electromotive force of the combination,

$$\text{Zn} - \text{ZnSO}_4 \,||\, \text{CuSO}_4 - \text{Cu}.$$

Since, according to Nernst's equation,

$$E = E^+ - E^- = \frac{RT}{2F}\ln\frac{p_1}{P_1} - \frac{RT}{2F}\ln\frac{p_2}{P_2},$$

where P_1 and p_1 refer to the copper, and P_2 and p_2 refer to the zinc, we have

$$E = E^+ - E^- = 0.308 - (-0.797) = 1.105 \text{ volts.}$$

Concentration Elements. We now proceed to consider cells in which the electromotive force depends primarily on differences in concentration, — the so-called "concentration elements."

Concentration elements may be conveniently divided into two classes: (a) *elements in which the electrodes are of different concentrations*, and (b) *elements in which the solutions are of different concentrations.*

(a) *Elements in which the Electrodes are of Different Concentrations. (Amalgams and Alloys.)*

Let us consider a concentration cell formed of two amalgams containing different concentrations of the same metal immersed in a solution of a salt of the metal. Such a cell may be represented by the following scheme:

M-amalgam concentrated c_2	MA	M-amalgam dilute c_1

In this cell let P_2 and c_2 denote the electrolytic solution pressure and the concentration, respectively, of the metal in the concentrated amalgam, while P_1 and c_1 represent the corresponding quantities for the dilute amalgam. Also let p represent the osmotic pressure of the solution of the salt, MA. The difference of potential at the point of contact of the concentrated amalgam and the solution will be

$$E^- = \frac{RT}{nF} \ln \frac{p}{P_2},$$

and, in like manner, the difference of potential at the point of contact of the dilute amalgam and the solution will be

$$E^+ = \frac{RT}{nF} \ln \frac{p}{P_1}.$$

Therefore, the electromotive force of the cell will be

$$E = E^+ - E^- = \frac{RT}{nF} \ln \frac{P_2}{P_1}. \qquad (16)$$

If the amalgams are dilute, the osmotic pressure of the dissolved metal will be proportional to the solution pressure of the electrode, and since osmotic pressure is proportional to concentration, we may replace P_1 and P_2, in the above formula, by the proportional terms, c_1 and c_2, the respective concentrations of the metal in the two electrodes. Hence, we have

$$E = \frac{RT}{nF} \ln \frac{c_2}{c_1}. \tag{17}$$

The accuracy of this equation has been fully established by the experiments of Meyer,* and Richards and Forbes.†

Meyer's results for zinc amalgams in solutions of zinc sulphate are given in the accompanying table.

E. M. F. OF ZINC AMALGAMS

T, degrees.	c_2	c_1	E (obs.).	E (calc.).
284.6	0.003366	0.00011305	0.0419	0.0416
291.0	0.003366	0.00011305	0.0433	0.0425
285.4	0.002280	0.0000608	0.0474	0.0475
333 0	0.002280	0 0000608	0.0520	0.0519

The agreement between the observed and calculated values of E is all that can be desired. That the above formula holds for zinc amalgams may be considered as a proof of the fact, that the zinc dissolves in the mercury as monatomic molecules. Thus, suppose the zinc to be present in the mercury in the form of diatomic molecules; then, while the electrical energy would be equal to $2FE$, the osmotic work required to develop this energy would be $\frac{1}{2} RT \ln \frac{c_2}{c_1}$, hence we should have

$$E = \frac{1}{2} \frac{RT}{2F} \ln \frac{c_2}{c_1}, \tag{18}$$

or, the calculated value of the electromotive force would be just one-half of the observed value. The mercury in the amalgam has been shown to exert no effect upon the electromotive force of the cell, so long as the dissolved metal has the greater potential.

* Zeit. phys. Chem., 7, 477 (1891).

† Publication of the Carnegie Institution, No. 56.

(b) *Elements in which the Solutions are of Different Concentrations.* In this type of cell we have two electrodes of the same metal immersed in solutions of different ionic concentrations of the metal. Hence, we may put $P_1 = P_2$ in the equation,

$$E = E^+ - E^- = \frac{RT}{nF} \ln \frac{p_2}{P_2} - \frac{RT}{nF} \ln \frac{p_1}{P_1},$$

which then takes the form,

$$E = \frac{RT}{nF} \ln \frac{p_2}{p_1}.$$

Since osmotic pressure is proportional to concentration, p_1 and p_2 may be replaced by the proportional terms, c_1 and c_2, and the foregoing equation becomes,

$$E = \frac{RT}{nF} \ln \frac{c_2}{c_1},$$

or

$$E = \frac{RT}{nF} \ln \frac{m_2\alpha_2}{m_1\alpha_1}, \tag{19}$$

where m_1 and m_2 are the molar concentrations of the two solutions, and α_1 and α_2 are the corresponding degrees of ionization. As an example of a concentration element of this class we may take the following:

$$\text{Ag} - 0.01 \text{ m } \text{AgNO}_3 \,||\, 0.1 \text{ m } \text{AgNO}_3 - \text{Ag}.$$

The degrees of ionization of the two solutions at 18° are as follows: — for 0.01 m $AgNO_3$, $\alpha = 0.93$, and for 0.1 m $AgNO_3$, $\alpha = 0.81$. Substituting in the equation,

$$E = 0.058 \log \frac{m_2\alpha_2}{m_1\alpha_1},$$

we have

$$E = 0.058 \log \frac{0.1 \times 0.81}{0.01 \times 0.93} = 0.0545 \text{ volt}.$$

The value of E, found by direct experiment, is 0.055 volt.

In the example just given, the electrodes are reversible with respect to the positive ion of the electrolyte. Such electrodes are known as *electrodes of the first type.* It is also possible to construct

cells with electrodes which are reversible with respect to the negative ion of the electrolyte. These are termed *electrodes of the second type.* The calomel electrode is an example of an electrode of this latter type. If positive electricity passes from the metal to the solution, the mercury combines with the Cl′ ions, forming mercurous chloride, and if positive electricity passes in the reverse direction, mercurous chloride is reduced to mercury. In other words, the electrode behaves like a chlorine electrode, giving up, or absorbing the element, according to the direction of the current. A typical combination involving an electrode of the second type is the following:

$$\mathrm{Ag - AgCl,\ 0.1\ m\ KCl \longrightarrow KNO_3 - 0.1\ m\ AgNO_3 - Ag.}$$

This particular combination was studied by Goodwin,* with a view to determining the solubility of silver chloride. If we assume a saturated solution of silver chloride to be completely ionized then the solubility product will be

$$c_{\mathrm{Ag}^{\cdot}} \times c_{\mathrm{Cl}} = s.$$

Since the concentrations of the two ions, Ag˙ and Cl′, are equal, it follows that $\sqrt{s}$ will be equal to the solubility of the silver chloride. The electromotive force of a concentration cell, at 25°, is given by the equation,

$$E = \frac{0.0595}{n} \log \frac{m_2\alpha_2}{m_1\alpha_1},$$

or

$$\log \frac{m_2\alpha_2}{m_1\alpha_1} = \frac{En}{0.0595}.$$

The value of E, at 25°, for the above cell was found to be 0.450 volt. The degrees of ionization of the two electrolytes are as follows: — for 0.1 molar $AgNO_3$, $\alpha = 0.82$, and 0.1 molar KCl, $\alpha = 0.85$. Substituting in the preceding equation, we obtain

$$\log \frac{0.1 \times 0.82}{c_1} = \frac{0.450}{0.0595},$$

therefore,

$$c_1 = 2.24 \times 10^{-9}.$$

* Zeit. phys. Chem., 13, 577 (1894).

Or, 2.24×10^{-9} is the concentration of the $Ag^{\cdot}$ ion in mols per liter in a 0.1 molar potassium chloride solution of silver chloride. Hence, the solubility product s will be

$$s = 2.24 \times 10^{-9} \times 0.085 = 1.91 \times 10^{-10},$$

and

$$\sqrt{s} = 1.38 \times 10^{-5};$$

that is, the solubility of silver chloride in a saturated aqueous solution is 1.38×10^{-5} mol per liter at 25°.

The Difference of Potential at the Junction of the Solutions of Two Electrolytes. Thus far we have not taken into consideration the potential differences which may be established at the junction of two solutions. Nernst* has shown, that in many cases it is possible to calculate these differences of potential by means of his osmotic theory of the origin of electromotive force, and the values thus obtained are in close agreement with the results of experiment. Let us imagine that two solutions of hydrochloric acid of different concentrations are brought together so as to avoid mixing, the acid in each solution being highly ionized. The hydrogen and chlorine ions will diffuse independently, and since the former move with the greater velocity, the more dilute solution will soon contain an excess of $H^{\cdot}$ ions and the more concentrated solution an excess of Cl' ions. The more dilute solution will become positively charged, owing to the presence of an excess of $H^{\cdot}$ ions, while the more concentrated solution will acquire a negative charge, due to the presence of an excess of Cl' ions. The accumulation of positive electricity, however, will retard the velocity of the $H^{\cdot}$ ions and accelerate the velocity of the Cl' ions, so that ultimately, the two ions will move with the same velocity. The difference of potential produced in this way will cease to exist when the two solutions have acquired the same concentration.

In general, it may be stated, that the difference of potential set up at the junction of the two solutions is caused by the difference in the rates of migration of the two ions, the more dilute solution acquiring a charge corresponding to that of the faster moving ion.

Electromotive Force of Concentration Cells with Transference. Let u and v be the migration velocities of the cation and the anion respectively, and let p_2 be the osmotic pressure of the ions in the concentrated solution, and p_1 the osmotic pressure of the

* Zeit. phys. Chem., 4, 129 (1889).

ions in the dilute solution. Now let n faraday of electricity pass from the concentrated solution to the dilute solution, then $\frac{u}{u+v}$ positive ions will migrate from the concentrated to the dilute solution, while $\frac{v}{u+v}$ negative ions will migrate from the dilute to the concentrated solution. The maximum work done by the process will be

$$\frac{u}{u+v} RT \ln \frac{p_2}{p_1} - \frac{v}{u+v} RT \ln \frac{p_2}{p_1} = \frac{u-v}{u+v} RT \ln \frac{p_2}{p_1}.$$

The corresponding electrical energy developed is EF, hence we have

$$E = \frac{u-v}{u+v} \cdot \frac{RT}{nF} \ln \frac{p_2}{p_1}, \tag{20}$$

or, since osmotic pressure is proportional to concentration, we may substitute c_1 and c_2 for p_1 and p_2, in the preceding equation, and obtain the following expression for the electromotive force at the junction of the two solutions: —

$$E = \frac{u-v}{u+v} \cdot \frac{RT}{nF} \ln \frac{c_2}{c_1}. \tag{21}$$

As an example of the use of the above formula, we may take the calculation of the electromotive force of the following combination: —

$$\underset{(a)}{\text{Ag}} - \text{0.01 m } \text{AgNO}_3 - \underset{(b)}{\text{0.1 m } \text{AgNO}_3} - \underset{(c)}{\text{Ag}}.$$

Taking the junctions (a), (b), and (c) in order, we obtain

$$E = \frac{RT}{nF} \ln \frac{C}{c_1} - \frac{u-v}{u+v} \cdot \frac{RT}{nF} \ln \frac{c_2}{c_1} - \frac{RT}{nF} \ln \frac{C}{c_2} *$$

$$= \frac{2v}{u+v} \cdot \frac{RT}{nF} \ln \frac{c_2}{c_1}.$$

But $\frac{2v}{u+v} = 2n_a$, the transference number of the anion, and therefore, we may write the preceding equation in the form,

$$E = 2n_a \frac{RT}{nF} \ln \frac{c_2}{c_1}. \tag{22}$$

* C is a number proportional to the solution pressure P.

Assuming the temperature to be 17°, and passing to Briggsian logarithms, we have

$$E = 0.116\, n_a \log \frac{c_2}{c_1}. \tag{23}$$

The transference number for the anion of silver nitrate is 0.522, while $c_2 = m_2\alpha_2 = 0.1 \times 0.82 = 0.082$, and $c_1 = m_1\alpha_1 = 0.01 \times 0.94 = 0.0094$. Hence,

$$E = 2 \times 0.522 \times 0.058 \times \log \frac{0.082}{0.0094},$$

or

$$E = 0.057 \text{ volt.}$$

The value found by direct experiment is 0.055 volt.

It is to be noted, that if the electromotive force at the junction of the two solutions is negative, equation (22) takes the form,

$$E = 2\, n_c \frac{RT}{nF} \ln \frac{c_2}{c_1}, \tag{24}$$

where n_c is the transference number of the cation.

Electromotive Force of Concentration Cells without Transference. A less familiar type of concentration cell is that which does not involve transference. The following combination may be taken as an example of such a cell:

$$\text{Ag} \mid \underset{c_1}{\text{AgCl, KCl}} \mid \text{K (Hg)}_4 \parallel \text{K (Hg)}_4 \mid \underset{c_2}{\text{KCl, AgCl}} \mid \text{Ag}.$$

It will be observed, that this cell is in reality made up of two independent cells, and involves no liquid junction. While the elimination of diffusion appreciably simplifies the theoretical treatment of cells of this type, practically, it is difficult to find electrodes which are reversible toward both ions of the electrolyte. The passage of one faraday of electricity through the cell results in the formation, on the dilute side, of one equivalent of potassium chloride, from the silver chloride and the amalgam, while on the concentrated side, a corresponding amount of potassium chloride is decomposed. If we assume the solutions to be so dilute as to be completely ionized, one equivalent of potassium chloride will

function as two mols, and the electromotive force of the cell will be

$$E = \frac{2\,RT}{nF} \ln \frac{c_2}{c_1}. \tag{25}$$

Formulas for the Difference of Potential at Liquid Junctions. As has been pointed out, the total electromotive force of a concentration cell with transference is made up of the algebraic sum of the potentials at the two electrodes, and the potential at the junction of the two solutions. Since the value of the potential at the electrodes alone is often desired, numerous formulas have been derived for the calculation of the potential at the liquid junction.

In addition to the formula of Nernst, already mentioned, formulas have been proposed by Planck,* Henderson,† Cumming,‡ Lewis and Sargent,§ and MacInnes.|| Of these different formulas, that of MacInnes possesses distinct advantages.

He has shown that the probable value of the electromotive force, E_L, of the liquid junction connecting differently concentrated solutions of the same salt, may be expressed by the equations

$$E_L = E(2\,n_c - 1)/2, \tag{26}$$

and

$$E_L = E_t(1 - 1/2\,n_c), \tag{27}$$

where E is the voltage of a concentration cell without transference and E_t that of a concentration cell with transference, each of the latter containing the solutions which are in contact at the liquid junction. It is to be observed, that equations (26) and (27) involve no assumptions concerning the concentrations of the ions in the solutions, one of the characteristics which distinguishes these formulas from any of the others hitherto proposed.

Lewis and Sargent¶ have proposed a modification of a formula derived by Planck, for the difference of potential at the junction of two equally concentrated electrolytes having a common ion. If Λ_1 and Λ_2 are the equivalent conductances of the two electrolytes,

* Wied. Ann., **40**, 561 (1890).
† Zeit. phys. Chem., **59**, 118 (1906); **63**, 325 (1908).
‡ Trans. Faraday Soc., **8**, 86 (1912); **9**, 174 (1913).
§ Jour. Am. Chem. Soc., **31**, 363 (1909).
|| Ibid., **37**, 2301 (1915).
¶ loc. cit.

the value of the liquid junction potential, E_L, is given by the formula,

$$E_L = \frac{RT}{F} \ln \frac{\Lambda_1}{\Lambda_2}. \qquad (28)$$

By the use of equations (26), (27), and (28), it is possible to calculate the junction-potential between the solutions of any two uni-univalent ionogens, to within a few tenths of a millivolt.

Whenever possible, however, liquid junctions should be entirely eliminated, thus removing the possibility of error due to the employment of correction formulas.

Flowing Junctions. The importance of renewing the surface at the junction of the solution of two electrolytes, in order to secure constant and reproducible differences of potential, has been emphasized by a number of investigators, notably by Walpole,* who pointed out that fairly constant values could be obtained by forming the junctions with tapes along which the solutions were permitted to flow.

Lamb and Larson† were the first, however, to develop a "flowing junction," by means of which differences of potential, constant and reproducible to within 0.01 millivolt, can be obtained. This result was secured by allowing an upward current of the denser electrolyte to meet a downward current of the lighter electrolyte, in a vertical tube at its point of union with a horizontal outflow tube, as is shown diagrammatically in Fig. 147. Recently MacInnes and Yeh,‡ employing a modified form of the Lamb and Larson flowing junction, have shown that the values of the junction potential, calculated by the formula of Lewis and Sargent, (equation (28)), are, in nearly every case, in excellent agreement with those found by direct experiment.

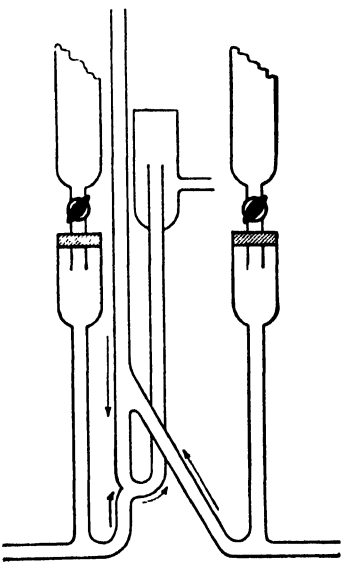


Fig. 147

* Jour. Chem. Soc., 105, 2521 (1914). † Jour. Am. Chem. Soc., 42, 229 (1920).
‡ Ibid., 43, 2563 (1921).

Normal Electrode Potential. The difference of potential at a reversible electrode, when the concentration of the ions of the electrolyte is molar, is known as the *normal electrode potential.*

According to Nernst, the expression for the difference of potential at a single electrode is

$$E = \frac{RT}{nF} \ln \frac{p}{P},$$

$$= \frac{RT}{nF} \ln \frac{c}{C}, \tag{29}$$

where P is the solution pressure of the electrode, p is the osmotic pressure of the ions of the electrolyte, and where C and c are concentrations proportional to P and p respectively. If the concentration of the ions is unity, $c = 1$, and the expression for the normal electrode potential, E_0, becomes

$$E_0 = \frac{RT}{nF} \ln \frac{1}{C}. \tag{30}$$

On subtracting (29) from (30), we obtain,

$$E_0 = E - \frac{RT}{nF} \ln c, \tag{31}$$

where c is the concentration of the ions in a solution whose electrode potential is E. In the actual determination of normal electrode potentials, the value of c, in equation (31), is usually very much less than unity.

The table on the following page gives the values of most important electrode potentials, the data in the second column being referred to the normal calomel electrode as zero, while the data of the third column is referred to the normal hydrogen electrode as zero.

Applications of Electromotive Force Measurements.

(1) *Electrometric Determination of Valence.* The equation of Nernst, for the electromotive force of a concentration cell, may be employed to determine the valence of the ions.

For example, the chemical behavior of mercurous salts is such as to justify the use of single or double formulas, involving either $Hg^{\cdot}$ or $Hg_2^{\cdot\cdot}$. To determine which of these two formulas is correct, Ogg* set up the following cell:

$$\begin{array}{ccc} Hg - 0.05 \text{ n Mercurous nitrate} & || & 0.5 \text{ n Mercurous nitrate} - Hg \\ 0.1 \text{ n } HNO_3 & & 0.1 \text{ n } HNO_3 \\ c_1 & & c_2 \end{array}$$

* Zeit. phys. Chem., 27, 285 (1898).

NORMAL ELECTRODE POTENTIALS AT 25° C.

Electrode.	Normal Calomel Electrode = 0.	Normal Hydrogen Electrode = 0.	Authority.
Li, $Li^{\cdot}$	−3.3044	−3.0222	Lewis & Kraus*
K, $K^{\cdot}$	−3.2078	−2.9256	Lewis & Keyes†
Na, $Na^{\cdot}$	−2.9975	−2.7153	Lewis & Kraus‡
Mg, $Mg^{\cdot\cdot}$(18°)	−2.148	−1.866	Beck§
Zn, $Zn^{\cdot\cdot}$	−1.0403	−0.7581	
Fe, $Fe^{\cdot\cdot}$	−0.723	−0.441	
Cd, $Cd^{\cdot\cdot}$	−0.6798	−0.3976	
Tl, $Tl^{\cdot}$	−0.6192	−0.3364	Richards & Smyth‖
Co, $Co^{\cdot\cdot}$	−0.573	−0.29	
Ni, $Ni^{\cdot\cdot}$	−0.50	−0.22	
Sn, $Sn^{\cdot\cdot}$	−0.418	−0.136	
Pb, $Pb^{\cdot\cdot}$	−0.4125	−0.1295	Getman¶
H_2, $H^{\cdot}$	−0.2822	±0.0000	
Bi, $Bi^{\cdot\cdot\cdot}$(18.5°)	−0.058	+0.226	Jellinek and Kuhn**
Cu, $Cu^{\cdot\cdot}$	+0.0612	+0.3448	Lewis & Lacey††
Te, $Te^{\cdot\cdot\cdot\cdot}$(18°)	+0.276	+0.558	Reichenstein‡‡
Hg, $Hg_2^{\cdot\cdot}$	+0.5164	+0.7986	
Ag, $Ag^{\cdot}$	+0.5173	+0.7995	Noyes and Brann§§
Te, Te'' (18°)	−1.109	−0.827	Reichenstein‡‡
S, S''	−0.79	−0.51	
O_2, OH'	+0.1154	+0.3976	Lewis & Kraus‡
I_2, I'	+0.2454	+0.5382	McKeown‖‖
Br_2, Br'	+0.7837	+1.0659	
Cl_2, Cl'	+1.0772	+1.3594	

* Lewis and Kraus, Jour. Am. Chem. Soc., **35**, 341 (1913).
† Lewis and Keyes, Ibid., **34**, 119 (1912).
‡ Lewis and Kraus, Ibid., **32**, 1459 (1910).
§ Beck, Rec. trav. chim., **41**, 353 (1922).
‖ Richards and Smyth, Jour. Am. Chem. Soc., **44**, 524 (1922).
¶ Getman, Ibid. **40**, 611 (1918).
** Jellinek and Kuhn, Zeit. phys. Chem., **105**, 337 (1923).
†† Lewis and Lacey, Jour. Am. Chem. Soc., **36**, 804 (1913).
‡‡ Reichenstein, Zeit. phys. Chem., **97**, 257 (1921).
§§ Noyes and Brann, Jour. Am. Chem. Soc., **34**, 1016 (1912).
‖‖ McKeown, Trans. Faraday Soc., **17**, 517 (1922).

For a complete summary of electrode potentials the student is referred to a paper by R. H. Gerke in Chemical Reviews, Vol. I, No. 4, p. 377.

and found its electromotive force, at 17°, to be 0.029 volt. If we neglect the difference of potential at the junction of the two solutions, the electromotive force of this cell may be calculated by the familiar formula,

$$E = \frac{RT}{nF} \ln \frac{c_2}{c_1}.$$

Assuming that $c_2/c_1 = 10$, and passing to Briggsian logarithms, we have

$$0.029 = 0.058\,/n,$$

or

$$n = 2.$$

Hence, the valence of the mercurous ion is 2 and it must, in consequence, be represented by $Hg_2^{\cdot\cdot}$. It follows that the correct formula of mercurous nitrate is $Hg_2(NO_3)_2$.

(2) *Electrometric Determination of Transference Numbers.* The formula for the electromotive force of a concentration cell with transference has been shown to be

$$E_t = \frac{2\,n_c RT}{nF} \ln \frac{c_2}{c_1}. \tag{32}$$

If the electromotive force of such a combination is measured, and the values of c_1 and c_2 are accurately known, obviously the value of the transference number of the cation, n_c, can be calculated. If, after having measured E_t, a similar cell without transference be set up, and its electromotive force measured, it is possible to obtain an expression for n_c which does not involve either c_1 or c_2. As has been shown, the electromotive force of a cell without transference, E, is given by the formula,

$$E = \frac{2\,RT}{nF} \ln \frac{c_2}{c_1}. \tag{33}$$

Dividing equation (32) by equation (33), we obtain

$$n_c = \frac{E_t}{E}, \tag{34}$$

which expression gives the transference number in terms of the two measured electromotive forces. This method for the determination of transference numbers was first suggested by Helmholtz.*

The transference number of the lithium ion has recently been determined in this manner by Pearce and Mortimer,† using cells made up according to the following schemes:

$$\text{Ag} \mid \text{AgCl, LiCl} \parallel \text{LiCl, AgCl} \mid \text{Ag (with transference)},$$

$$\underset{c_1}{\text{Ag} \mid \text{AgCl, LiCl} \mid \text{Li (Hg)}_x} \parallel \underset{c_2}{\text{Li (Hg)}_x \mid \text{LiCl, AgCl} \mid \text{Ag}} \text{ (without transference).}$$

* Ges. Abhl. I, 840: II, 979.

† Jour. Am. Chem. Soc., 40, 518 (1918).

A comparison between their results and the values given by Kohlrausch and Holborn* is afforded by the accompanying table.

Concentration Ratio.....	1.0–0.1	0.5–0.05	0.1–0.01	0.05–0.005
Mean n_c (K. and H.).....	0.285	0.300	0.340	0.360
Mean n_c (P. and M.).....	0.279	0.322	0.343	0.365

It will be observed that the agreement between the two series of results is satisfactory.

Later determinations of the transference numbers of lithium chloride solutions, by MacInnes and Beattie,† are given in the accompanying table.

TRANSFERENCE NUMBERS OF LITHIUM ION IN LITHIUM CHLORIDE

Concentration.	E.m.f. Method.	"Best value" Hittorf Method.
0.001	0.359	.....
0.005	0.341	.....
0.01	0.334	0.332
0.02	0.327	0.328
0.05	0.318	0.320
0.10	0.311	0.313
0.20	0.304	0.304
0.30	0.299	0.299
0.50	0.293	.....
1.0	0.286	.....
2.0	0.276	.....
3.0	0.268	.....

These results have been shown to be in close agreement with the direct transference measurements of Jahn, Bein, and Washburn.

(3) *Ionization of Water.* An important application of the gas cell is its use in determining the degree of ionization of water. If we measure the electromotive force of the cell,

$$Pt_{H_2} - 0.1\ m\ NaOH - 0.1\ m\ HCl - Pt_{H_2},$$

$$\longrightarrow$$

and determine the concentration of the $H^{\cdot}$ ions on one side, and the concentration of the OH' ions on the other side, we can calculate the concentration of the $H^{\cdot}$ ions in the sodium hydroxide

* Leitvermögen der Elektrolyte, p. 201.

† Jour. Am. Chem. Soc., **42**, 1117 (1920).

solution. The reaction which produces the current is represented by the equation,

$$NaOH + HCl = NaCl + H_2O,$$

or more correctly,

$$H^{\cdot} + OH' = H_2O.$$

The electromotive force of the above cell is 0.646 volt, at 25°. At the junction of the two solutions, an electromotive force of 0.0468 volt is set up; hence, the true electromotive force of the cell is 0.646 + 0.0468 = 0.6928 volt. The degree of ionization of a 0.1 molar solution of hydrochloric acid is $\alpha_1 = 0.847$, and the degree of ionization of a 0.1 molar solution of sodium hydroxide is $\alpha_2 = 0.924$. Introducing these values into the Nernst equation,

$$E = \frac{RT}{nF} \ln \frac{c_2}{c_1},$$

we have

$$0.6928 = 0.0595 \log \frac{0.1 \times 0.924}{c_1}.$$

Solving this equation, we find c_1 to be equal to 1.66×10^{-13}. Therefore,

$$s = c_{H^{\cdot}} \times c_{OH'} = 1.66 \times 10^{-13} \times 0.1 \times 0.847 = 1.406 \times 10^{-14},$$

and

$$c_{H^{\cdot}} = c_{OH'} = \sqrt{s} = \sqrt{1.406 \times 10^{-14}} = 1.187 \times 10^{-7}.$$

This value is in excellent agreement with the values obtained by various other methods, as shown in the table on p. 522.

When we consider the exceedingly small extent to which water is ionized, the close agreement between these results is most satisfactory. The correctness of these figures can be further checked by taking the values of the degree of ionization of water at two temperatures, and calculating the heat of the reaction,

$$H^{\cdot} + OH' = H_2O,$$

by means of the equation of the reaction isochore. Thus, according to Kohlrausch, the degree of ionization of water is 0.35×10^{-7},

at 0°, and 2.48×10^{-7}, at 50°. Introducing these values into the equation,

$$-Q = \frac{2.3026\, R\, (\log K_2 - \log K_1)\, T_1 T_2}{T_2 - T_1},$$

and solving for Q, we obtain $-13{,}810$ calories. This value agrees well with that found by the direct measurement of the heat of neutralization of completely ionized acids and bases, viz., $-13{,}800$ calories.

(4) *Gas Electrodes — The Hydrogen Electrode.* It is interesting to note, that gases may function as electrodes, in much the same way as metals or amalgams. Gas electrodes are usually prepared by partially immersing strips of platinized platinum in a solution of a suitable electrolyte, and bubbling the gas through the solution until a constant difference of potential is established between it and the electrode. A very satisfactory form of gas electrode is shown in Fig. 148.

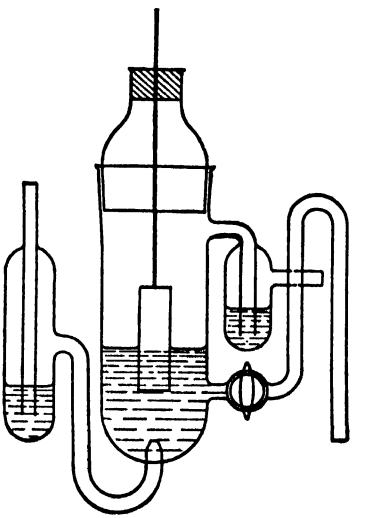


Fig. 148

As a result of the investigations of Le Blanc and others,* gas electrodes have been shown to be completely reversible and to resemble ordinary metallic electrodes in their electromotive behavior. Thus, hydrogen, oxygen, chlorine, hydrogen sulphide and carbon monoxide have been found to function as gas electrodes when bubbled over the surface of strips of platinized platinum immersed in solutions of the proper electrolytes.†

Reference has already been made to the hydrogen electrode in connection with the measurement of single electrode potentials.

* Le Blanc, Zeit. phys. Chem., **12**, 333 (1893); Böttger, Ibid., **24**, 253 (1897); Wilsmore, Ibid., **35**, 291 (1900); Bose, Ibid., **34**, 701 (1900); **38**, 1 (1901).

† Bernfeld, Zeit. phys. Chem., **25**, 46 (1898); Hoffmann and Wurthmann, Berichte, **52**, 1185 (1919).

This electrode is completely reversible and behaves like a plate of metallic hydrogen, the reaction at the electrode being represented by the equation,

$$H_2 + 2\,(+) \rightleftarrows 2\,H^{\cdot}.$$

The amount of energy developed by the passage of a certain quantity of gas into the ionic state is precisely the quantity necessary and sufficient to produce the reverse action. This being true, the metal of the electrode can exert no influence upon the electromotive force.

A hydrogen concentration cell can be formed by connecting two hydrogen electrodes, containing the gas at different pressures, through an intermediate electrolyte. The direction of the current is such, that the pressures on the two sides of the cell tend to become equal, molecular hydrogen being ionized on the high pressure side, and ionized hydrogen being discharged on the low pressure side. The electromotive force of such a cell can be calculated by means of the Nernst equation. Let us consider a cell composed of two hydrogen electrodes, each at atmospheric pressure, the $H^{\cdot}$ ion concentration in each being c_1, then

$$E = \frac{RT}{2F}\ln\frac{c_1}{C_1} - \frac{RT}{2F}\ln\frac{c_1}{C_1} = 0,$$

where C_1 is the molecular concentration of the hydrogen dissolved in the platinum, at gaseous pressure p_1. Since the hydrogen is present in the form of diatomic molecules, $n = 2$. If now the pressure of the gas at one electrode be increased to p_2, and the corresponding molecular concentration of the hydrogen in the electrode be C_2, then we shall have

$$E = \frac{RT}{2F}\ln\frac{c_1}{C_1} - \frac{RT}{2F}\ln\frac{c_1}{C_2},$$

or, since

$$C_1 : C_2 :: p_1 : p_2,$$

$$E = \frac{RT}{2F}\ln\frac{p_2}{p_1}. \tag{35}$$

Equation (35) applies equally well to cells in which two different gases are employed.

The hydrogen ion concentration of a solution can readily be

calculated from the measured value of the electromotive force of a cell made up according to the following scheme:

$$H_2 - \text{Solution} - \text{Saturated KCl} - \text{m KCl, HgCl} - \text{Hg}.$$

The relation between the unknown hydrogen ion concentration, c_H, and the electromotive force of the cell, at 25°, is given by the equation of Nernst,

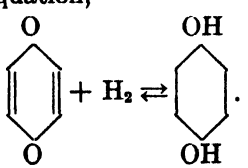
$$E = 0.059 \log_{10} \frac{1}{c_H} + 0.282 \qquad (36)$$

where +0.282 volt is the potential of the normal calomel electrode referred to the hydrogen electrode as zero.

Therefore, in order to determine the hydrogen ion concentration of a solution, a hydrogen electrode is immersed in the solution, and the electromotive force of the cell, formed by connecting the solution with a calomel electrode, is measured. On substituting the value of the electromotive force, thus determined, in equation (36), the value of the hydrogen ion concentration, c_H, can be easily calculated.

In the derivation of equation (36) it was assumed that no boundary electromotive force existed. The interposition of a saturated solution of potassium chloride, as indicated above, as a rule either minimizes or entirely eliminates any existing junction potential. It is furthermore of importance to insure that the electrode is supplied with pure hydrogen at atmospheric pressure.

An exceedingly simple and useful substitute for the hydrogen electrode is the quinhydrone electrode of Biilmann.* Quinhydrone is the addition product resulting from the mixture of one mol of quinone with one mol of hydroquinone. The substance can be readily prepared in a pure condition by mixing alcoholic solutions of quinone and hydroquinone in equimolecular proportions and then pouring the resulting solution into cold water. The saturated aqueous solution of quinhydrone is approximately 0.005 molal. The condition of equilibrium within this solution is represented by the equation,



* Biilmann, Ann. chim. phys. (9), 15, 109 (1921); 16, 321 (1921).

According to the law of mass action,

$$\frac{c_{C_6H_4O_2} \cdot c_{H_2}}{c_{C_6H_4(OH)_2}} K,$$

or

$$c_{H_2} = K \cdot \frac{c_{C_6H_4(OH)_2}}{c_{C_6H_4O_2}},$$

but the concentrations of the quinone and hydroquinone are equal, hence

$$c_{H_2} = K.$$

On dipping a platinum or a gold electrode into a saturated solution of quinhydrone a well-defined and reproducible difference of potential is established. When measured against a hydrogen electrode of equal hydrogen ion concentration, the potential of the quinhydrone electrode is approximately +0.7 volt. The quinhydrone electrode can be employed in place of the hydrogen electrode in acid solutions, but not in alkaline solutions in which the hydrogen ion concentration is less than 1×10^{-8}. Furthermore, it cannot be depended upon to give accurate results in solutions of electrolytes in which the concentration exceeds 0.1 mol per liter. These limitations are easily removed, however, by shaking the electrode solution with an excess of either one of the components, quinone or hydroquinone. The exact values of the potential of the quinhydrone electrode under different conditions are as follows:

0.005 m quinhydrone	0.7044 volt (18°)
0.005 m quinhydrone	0.6990 volt (25°)
0.005 m quinhydrone + quinone	0.7570 volt (18°)
0.005 m quinhydrone + hydroquinone	0.6185 volt (18°)

Hydrogen ion concentrations are commonly expressed by bacteriologists and biochemists in terms of the negative exponents of the actual hydrogen ion concentrations. Sörensen,* who first proposed this method of expressing hydrogen ion concentration, recommended the symbol P_{H^+}, but the subsequent suggestion of

* Sörensen, Biochem. Zeit., 21, 131 (1909).

Clark,* that hydrogen ion concentration be denoted by the symbol pH has been practically universally adopted because of its greater simplicity. The relation of pH to hydrogen ion concentration, as hitherto expressed by the symbol $c_{H^\cdot}$, is indicated by the equation,

$$pH = \log \frac{1}{c_{H^\cdot}}, \quad \text{or} \quad c_{H^\cdot} = 1 \times 10^{-pH}. \tag{37}$$

Thus, in a solution where $c_{H^\cdot} = 2 \times 10^{-4}$, the value of pH is

$$pH = \log \frac{1}{2 \times 10^{-4}} = 3.699.$$

As has been shown in the preceding section, pure water undergoes dissociation into hydrogen and hydroxyl ions according to the equation,

$$H \cdot OH = H^\cdot + OH',$$

and therefore,

$$\frac{c_{H^\cdot} \times c_{OH'}}{c_{H_2O}} \quad K.$$

The approximate value of K, at temperatures ranging from 20° C. to 25° C., is 1×10^{-14}. If the normal concentration of hydroxyl ions in water is increased by the addition of a base, the concentration of hydrogen ions will experience a corresponding decrease, in order that the value of the equilibrium constant, K, shall remain constant. Thus, if in the aqueous solution of a base, the concentration of the hydroxyl ions is 1×10^{-4}, the concentration of the hydrogen ions must be

$$c_{H^\cdot} = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10},$$

or $pH = 10$. Since at ordinary temperatures, $K = 1 \times 10^{-14}$, we may write

$$pH + pOH = 14.$$

The following table, in which are included the approximate values of $c_{H^\cdot}$ and pH for a few solutions of common electrolytes, will help to familiarize the student with the significance of the Sörensen notation.

* Clark, " The Determination of Hydrogen Ions."

c_{H^+} AND *pH* VALUES OF COMMON ACIDS AND BASES

Solute.	Conc.	c_{H^+}	*pH*
HCl	1.0 n	8.0×10^{-1}	0.10
HCl	0.1 n	8.4×10^{-2}	1.07
HCl	0.01 n	9.5×10^{-3}	2.02
NaOH	1.0 n	0.90×10^{-14}	14.05
NaOH	0.1 n	0.86×10^{-13}	13.07
NaOH	0.01 n	0.76×10^{-12}	12.12
CH_3COOH	0.1 n	1.36×10^{-3}	2.87
NH_4OH	0.1 n	5.4×10^{-12}	11.27

(5) *Electrometric Titration.* Since the neutralization of acids and bases is accompanied by changes in the concentration of hydrogen and hydroxyl ions, it is apparent that the hydrogen electrode can be employed in place of an indicator in acidimetric and alkalimetric titrations. The first application of the hydrogen electrode to the titration of acids and bases was made by Böttger,* who showed that the method was applicable to titrations where ordinary indicators fail to give satisfactory results, as for example, in the titration of deeply colored, or turbid solutions.

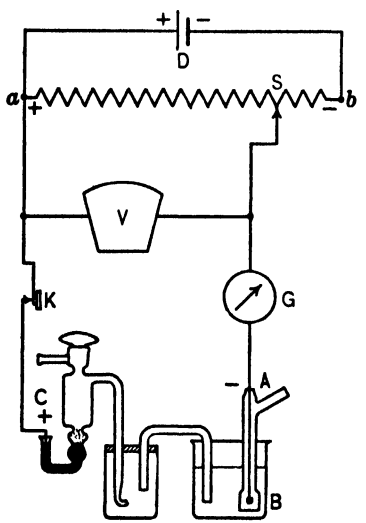


Fig. 149

Subsequently Böttger's method was modified by Hildebrand† who, by substituting a voltmeter for the potentiometer used by Böttger, greatly simplified the procedure of electrometric titration. The arrangement of the apparatus in Hildebrand's method is shown diagrammatically in Fig. 149. The beaker, *B*, contains the solution of which the hydrogen ion concentration is sought; into this solution the hydrogen electrode, *A*, and the side-tube of a calomel electrode, *C*, are introduced. The two electrodes are

* Zeit. phys. Chem., **24**, 253 (1897).

† Hildebrand, Jour. Am. Chem. Soc., **35**, 847 (1913).

connected to a battery, D, through a galvanometer, G. The electromotive force of the cell thus formed is balanced against a variable fraction of the electromotive force of the battery, D, by moving the sliding contact, S, along the resistance, ab, until a point is found where, on closing the key, K, no deflection is noted on the galvanometer. The voltmeter, V, serves to indicate the fall of potential from a to S, and, when the point of balance is found, the reading of the voltmeter corresponds to the electromotive force of the cell. Since in a neutral solution, the concentrations of both hydrogen and hydroxyl ions are identical, and equal to 1×10^{-7}, it follows that the end-point of the titration will correspond to a reading on the voltmeter of

$$E = 0.059 \log \frac{1}{1 \times 10^{-7}} + 0.282 = 0.695 \text{ volt.}$$

Numerous forms of hydrogen electrodes have been devised but those shown in Fig. 150 are among the most satisfactory.

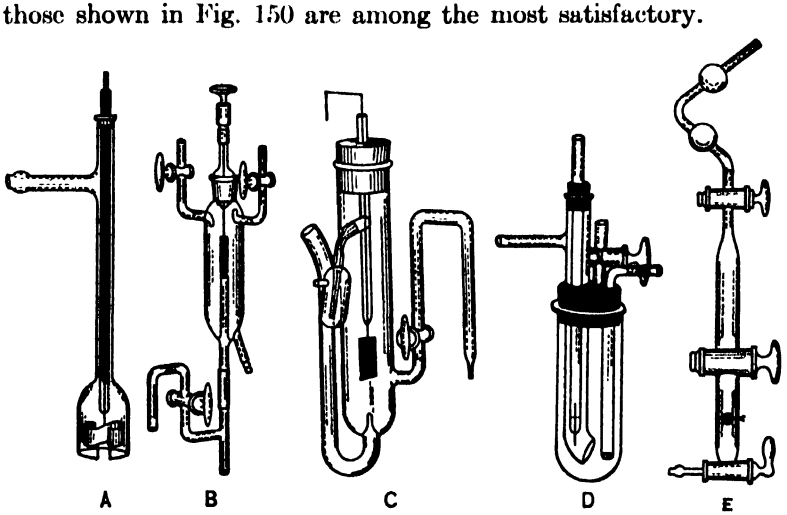


Fig. 150

In carrying out a titration of an acid solution with Hildebrand's apparatus, a solution of standard alkali is run into the beaker, B, in successive portions from a burette. After the addition of each portion of alkali, the electromotive force of the cell is measured and the reading of the voltmeter plotted against the corresponding burette reading. The amount of alkali required to neutralize

the acid is determined by reading from the resulting graph the number of cubic centimeters of standard alkali which correspond to 0.695 volt.

The results of the titration of hydrochloric and acetic acids by sodium hydroxide are shown graphically in Fig. 151, where the abscissae represent the number of cubic centimeters of sodium

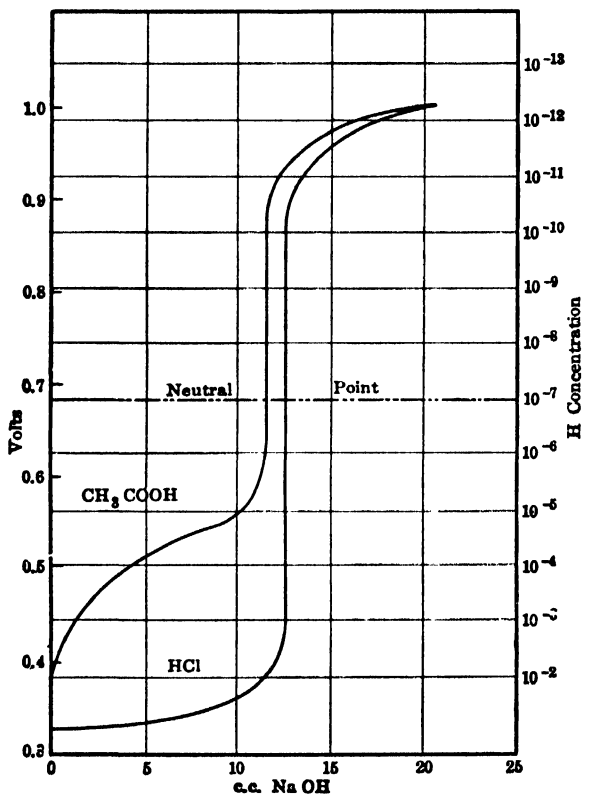


Fig. 151

hydroxide added to the solution from a burette, and where the ordinates represent the corresponding values of the electromotive force. The scale of hydrogen ion concentrations, at the right of the diagram, is calculated by means of equation (36). It will be seen that, in both cases, a sharp break occurs in the curves when the end-point of the titration is reached. Furthermore, acetic acid shows an initial electromotive force much greater than hydro-

chloric acid, corresponding to the fact that the hydrogen ion concentration is much less. It should be noticed that the first additions of alkali cause a marked decrease in acidity. This shows the effect of the acetate ion in diminishing the acidity of acetic acid. According to the law of mass action we have,

$$CH_3COOH \rightleftarrows CH_3COO' + H',$$

and since the concentration of CH_3COO', which was initially small, due to the slight ionization of the acid, is greatly increased by the addition of alkali, it follows that a corresponding diminution in the concentration of H' must occur. This effect is of sufficient magnitude to cause the acidity to decrease very slowly until the neutral point is reached, when a sudden change to alkaline reaction takes place. It can be shown, that the middle point of this portion of the curve corresponds to the normal salt, when both acid and base are present in exactly equivalent amounts. It will be observed, however, that this point at which acid and base are equivalent does not correspond to a neutral, but to an alkaline solution. This is in accord with the well-known fact, that sodium acetate solutions are hydrolyzed and react alkaline.

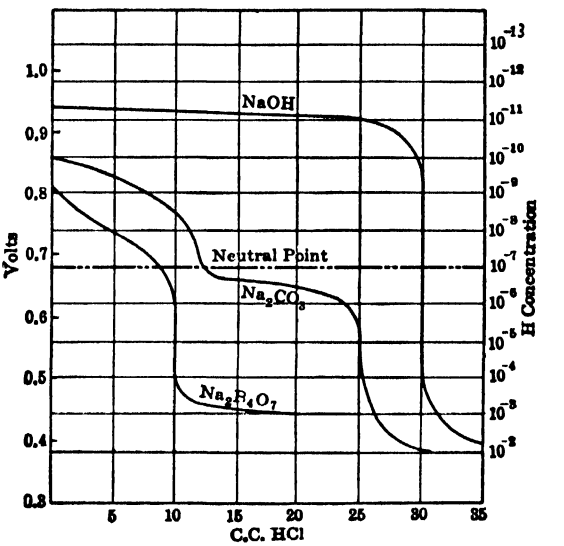


Fig. 152

Similar curves showing the variation in *pH* on titrating some typical alkaline solutions with hydrochloric acid are plotted in Fig. 152.

In many of the reactions upon which standard quantitative procedures are based, marked changes in hydrogen ion concentration occur. The feasibility of employing the hydrogen electrode to

determine the end-points in many of these reactions was first pointed out by Hildebrand and Harned,* and subsequently the application of the method was further extended by Hildebrand.† For example, it was found that a fairly accurate and rapid determination of magnesia in dolomite could be made in this manner. The curve shown in Fig. 153 represents the results of a typical

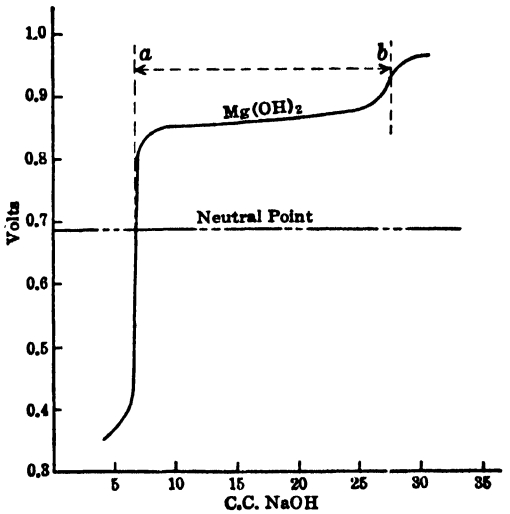


Fig. 153

titration of an acid solution of dolomite with sodium hydroxide. The horizontal distance between the inflections, indicated by the dotted line, *ab*, corresponds to the number of cubic centimeters of standard alkali required to effect the precipitation of the magnesium as hydroxide. The uncertainty which obtains in determining the exact position of the point, *b*, owing to the absence of a sharp inflection in the curve, may be removed by recourse to the method of Hostetter and Roberts‡ who showed that if the rate of change of *pH*, $\Delta p\mathrm{H}/\Delta v$, be plotted against the corresponding change in volume of standard alkali, Δv, a well-defined maximum is obtained at the end-point. The abrupt initial rise in the titra-

* Hildebrand and Harned, Proc. 8th Internat. Cong. App. Chem., 4, 217 (1912).

† Hildebrand, Jour. Am. Chem. Soc., 35, 847 (1913).

‡ Hostetter and Roberts, Ibid., 41, 1341 (1919).

tion curve corresponds to the neutralization of the excess of acid employed to dissolve the sample of dolomite, together with the amount of alkali required to precipitate the iron.

The hydrogen electrode has proven of great value to the analytical chemist in enabling him to determine the limiting ranges of *pH* which may be employed in both precipitations and separations. As an example of its use in this direction, the investigation of Fales and Ware* on the optimum conditions for the precipitation of zinc sulphide may be cited.

Electrometric titration has in recent years found extensive applications in the control of many industrial processes and its use is constantly being extended.†

Buffer Solutions. If a single drop of 0.1 m HCl be added to a liter of pure water, an enormous increase in the hydrogen ion concentration will occur immediately. In like manner, the addition of a drop of 0.1 m KOH to a liter of pure water will cause a correspondingly large increase in the hydroxyl ion concentration. From these facts it appears, that pure water alone is incapable of neutralizing even traces of acids and bases. It is to this lack of reserve neutralizing power, that the difficulty of preparing and preserving water having a hydrogen ion concentration of 1×10^{-7} equivalents per liter is to be ascribed.

It has been shown that any solution containing a weak acid together with one of its salts, or a weak base with one of its salts, is capable of neutralizing both acids and bases, within certain limits. This property of certain solutions of resisting change in hydrogen ion concentration, on the addition of acid or alkali, is known as *buffer action*, and the solutions are called *buffer solutions*.‡

The explanation of buffer action is relatively simple. If to a solution containing a weak acid, HA, and one of its salts, MA, there be added a small amount of an acid or base, the solution

* Fales and Ware, Jour. Am. Chem. Soc., **41**, 487 (1919).

† Keeler, Jour. Ind. Eng. Chem., **14**, 395 (1922); Klopsteg, Ibid., **14**, 399 (1922); Kolthoff, Rec. trav. chim., **39**, 280 (1922); Zeit. anorg. Chem., **112**, 155 (1920); Zeit. anal. Chem., **61**, 369 (1922); Auerbach and Smolezyk, Zeit. phys. Chem., **110**, 65 (1924); Bartell, Jour. Am. Chem. Soc., **39**, 630 (1917); Bovie, Ibid., **44**, 2892 (1922); Sharp and MacDougall, Ibid., **44**, 1193 (1922); Waters, Jour. Soc. Chem. Ind., **41**, 23371 (1922).

‡ According to Clark (loc. cit.) the term "buffer" is a corruption of the German word "*puffer*" meaning tampon.

will protect itself by neutralizing the added substance according to the following reactions:

$$A' + H^{\cdot} = HA,$$

and

$$HA + OH' = H_2O + A'.$$

It follows, therefore, if the reserve acidity is to be equal to the reserve alkalinity, that the concentration of A′ must be equal to the concentration of HA. But, according to the law of mass action,

$$c_{H^{\cdot}} = \frac{c_{HA}}{c_{A'}} K_A,$$

hence

$$c_{H^{\cdot}} = K_A.$$

That is, if the reserve acidity is equal to the reserve alkalinity, the ionization constant of the acid will be numerically equal to the hydrogen ion concentration of the solution.

The *pH* value of a buffer solution is established by introducing the solution into the beaker, *B*, of a cell similar to that shown in Fig. 149, and measuring the electromotive force. The value of *pH* is then calculated by substituting in equation (36) the value of the electromotive force of the cell, after having applied suitable corrections for junction potential and deviations of hydrogen pressure from normal atmospheric pressure. In this manner the graded *pH* values of the series of buffer solutions given in the following table were determined.

A number of standard buffer solutions have been described by Sörensen, Palitzsch, Walpole, and Clark and Lubs.* These solutions have been prepared with great care and their hydrogen ion concentrations accurately determined by hydrogen electrode measurements. These standard buffer solutions are very useful in the preparation of solutions of definite hydrogen ion concentrations. Thus, if it is desired to titrate a solution to some particular p_H value, we select from a table of standard buffer solutions, a formula which will give a solution of the desired hydrogen ion concentration. The carefully prepared buffer solution is introduced into an electrode vessel, and the solution to be titrated into a second similar vessel, while connection between the two solutions is established through an intermediate saturated solution of potassium chloride. A hydrogen electrode is immersed in each

* See "Determination of Hydrogen Ions," Clark, pp. 69 to 83 incl.

pH VALUES OF A SERIES OF TYPICAL BUFFER SOLUTIONS

No. of cc. of			No. of cc. of		
pH	0.2 m Na_2HPO_4	0.1 m citric acid	*pH*	0.2 m Na_2HPO_4	0.1 m citric acid
2.2	0.40	19.60	5.2	10.72	9.28
2.4	1.24	18.76	5.4	11.15	8.85
2.6	2.18	17.82	5.6	11.60	8.40
2.8	3.17	16.83	5.8	12.09	7.91
3.0	4.11	15.89	6.0	12.63	7.37
3.2	4.94	15.06	6.2	13.22	6.78
3.4	5.70	14.30	6.4	13.85	6.15
3.6	6.44	13.56	6.6	14.55	5.45
3.8	7.10	12.90	6.8	15.45	4.55
4.0	7.71	12.29	7.0	16.47	3.53
4.2	8.28	11.72	7.2	17.39	2.61
4.4	8.82	11.18	7.4	18.17	1.83
4.6	9.35	10.65	7.6	18.73	1.27
4.8	9.86	10.14	7.8	19.15	0.85
5.0	10.30	9.70	8.0	19.45	0.55

of the two solutions, and the cell thus formed is included in a circuit containing a galvanometer and appropriate keys. A small portion of the titrating solution is now added from a burette, and the deflection of the galvanometer noted. The titration is continued in this manner until, upon closing the circuit, the galvanometer shows no deflection. When this condition obtains, the two electrodes are manifestly at the same potential, and therefore, the two solutions must have identical hydrogen ion concentrations. The accuracy of the p_H value attainable by this method is entirely dependent upon the accuracy of the p_H value of the standard buffer solution.

Buffer solutions are now widely used as standards in color titrations, inasmuch as different indicators show characteristic colors at different hydrogen ion concentrations (see Clark, loc. cit.).

(6) *Electrometric Determination of Hydrolysis.* One of the most satisfactory methods which we possess for the determination of the degree of hydrolysis of salts depends upon the measurement of the electromotive force of cells made up as follows:

$$Pt_{H_2} \mid \text{salt solution} \mid \text{sat. } NH_4NO_3{}^* \parallel \text{N KCl, } Hg_2Cl_2 \mid Hg.$$

* A saturated solution of ammonium nitrate is interposed between the solutions to eliminate any difference of potential at the junction of the solutions.

From the measured electromotive force of the cell, the concentration of the hydrogen ion in the solution is determined, and from this the degree of hydrolytic dissociation of the salt can be calculated. The method is especially valuable in cases where the concentration of the hydrogen ion is very small. Unfortunately, the application of the method is restricted to the salts of metals less noble than hydrogen. In other words, it cannot be used to determine the hydrolysis of the salts of metals which would be precipitated upon the platinum electrode. The applicability of the method is further limited by the fact, that certain ions, such as $Fe^{\cdots}$, NO_3', and ClO_3', are either wholly, or partially reduced by the hydrogen of the hydrogen electrode.

The method has been successfully applied, by Denham,* to the determination of the hydrolysis of various salts, among which may be mentioned, aluminium chloride, aluminium sulphate, nickel chloride, nickel sulphate, cobalt sulphate, and ammonium chloride. As an illustration of the method, we may take the case of ammonium chloride which dissociates hydrolytically, according to the equation,

$$NH_4Cl + H \cdot OH \rightleftarrows NH_4OH + HCl.$$

Here we have a weak base and a very strong acid, as the products of hydrolytic dissociation. While the ammonium hydroxide may be regarded as practically non-ionized, the hydrochloric acid is to be considered as having undergone complete ionization. If one mol of ammonium chloride is dissolved in v liters of water, and the degree of hydrolytic dissociation is x, then the concentrations of the products of the reaction, ammonium hydroxide and hydrochloric acid, will be x/v. Since the acid is completely ionized, x/v will also represent the concentrations of the hydrogen and chloride ions. Assuming that the active mass of the water remains constant, we have, according to the law of mass action,

$$K_h = \frac{x^2}{v(1-x)},$$

where K_h is the hydrolytic constant. Since v is known, it only remains to determine x/v, or the concentration of the hydrogen ions, in order to be able to calculate K_h. The con-

* Jour. Chem. Soc., 93, 41 (1908); Zeit. anorg. Chem., 57, 361 (1908).

centration of the hydrogen ions may then be determined by means of equation (36),

$$E = 0.059 \log \frac{1}{c_{H^\cdot}} + 0.2822.$$

Substituting the electromotive force of the cell, 0.6056 volts, in this equation, we have

$$\log \frac{1}{c_{H^\cdot}} = \frac{0.6056 - 0.2822}{0.059},$$

or

$$\log c_{H^\cdot} = -5.4813.$$

Hence

$$c_{H^\cdot} = 3.301 \times 10^{-6}.$$

But $c_{H^\cdot} = \frac{x}{v}$, and therefore $x = 3.301 \times 10^{-6} \times 32, = 0.000109$.

The value of the hydrolytic constant is given by the equation

$$K_h = \frac{x^2}{v(1-x)} = \frac{(0.000106)^2}{32\,(1 - 0.000106)} = 3.5 \times 10^{-10}.$$

(7) *Chemical Cells.* The source of the electromotive force in concentration cells is the diffusion of the electrolyte, from a region of higher, to a region of lower concentration. In this process, there is nothing which can be characterized as a chemical change. On the other hand, there are numerous galvanic combinations in which the electromotive force is due, primarily, to chemical reactions within the cells. One of the most familiar examples of this type of cell is the Daniell cell, which may be represented by the following scheme:

$$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu.$$

The reaction taking place within the cell may be written ionically as follows:

$$Zn + Cu^{\cdot\cdot} \rightarrow Zn^{\cdot\cdot} + Cu,$$

and the equilibrium constant may be expressed by the equation,

$$K' = \frac{c'_{Zn^{\cdot\cdot}} \times c'_{Cu}}{c'_{Cu^{\cdot\cdot}} \times c'_{Zn}}, \qquad (38)$$

where the terms involving c' denote equilibrium concentrations. Since the concentrations of the solid metals are obviously constant, equation (38) may be simplified as follows:

$$K = \frac{c'_{Zn^{\cdot\cdot}}}{c'_{Cu^{\cdot\cdot}}}. \tag{39}$$

If $E_{0_{Zn}}$ and $E_{0_{Cu}}$ denote the normal electrode potentials of zinc and copper, respectively, then according to equation (31) we will have

$$E_{0_{Zn}} = E_{Zn} - \frac{RT}{nF} \ln c_{Zn^{\cdot\cdot}}, \tag{40}$$

and

$$E_{0_{Cu}} = E_{Cu} - \frac{RT}{nF} \ln c_{Cu^{\cdot\cdot}}. \tag{41}$$

Therefore, the total electromotive force of the cell will be

$$E = E_{Cu} - E_{Zn} = E_{0_{Cu}} - E_{0_{Zn}} - \frac{RT}{nF} \ln \frac{c_{Zn^{\cdot\cdot}}}{c_{Cu^{\cdot\cdot}}}. \tag{42}$$

When the four substances Zn, Cu, $Zn^{\cdot\cdot}$ and $Cu^{\cdot\cdot}$ are in equilibrium, equation (42) may be written in the form,

$$E = \frac{RT}{2F} \ln K - \frac{RT}{2F} \ln \frac{c_{Zn^{\cdot\cdot}}}{c_{Cu^{\cdot\cdot}}}, \tag{43}$$

since $n = 2$.

According to van't Hoff, the maximum work which can be derived from a given chemical reaction at constant temperature is given by the expression,

$$W = RT \ln K - RT \Sigma n \ln C, \text{ (see p. 369)} \tag{44}$$

where $\Sigma n = n_1' + n_2' + \cdots - n_1 - n_2 - \cdots$ in the general reaction equation,

$$n_1 A_1 + n_2 A_2 + \cdots = n_1' A_1' + n_2' A_2' + \cdots,$$

and where C denotes all the arbitrary concentration terms.

If the concentrations of the zinc and copper ions are $c_{Zn^{\cdot\cdot}}$ and $c_{Cu^{\cdot\cdot}}$, respectively, then the maximum work obtainable from the reaction taking place within the Daniell cell will be, according to equation (44),

$$W = 2EF = RT \ln \frac{c'_{Zn^{\cdot\cdot}}}{c'_{Cu^{\cdot\cdot}}} - RT \ln \frac{c_{Zn^{\cdot\cdot}}}{c_{Cu^{\cdot\cdot}}}. \tag{45}$$

If the concentrations of the solutions of the sulphates of zinc and copper be so chosen that the concentrations of the ions are equal, then the second term of equation (45) vanishes, and we have

$$W = 2EF = RT \ln K. \tag{46}$$

Since at 25°, $E = 1.1$ volt approximately, we may substitute these values in equation (46), and evaluate the equilibrium constant, K, as follows:

$$\log K = \frac{2 \times 1.1}{0.059} = 37,$$

or

$$K = 10^{37}.$$

That is, when equilibrium is established, the concentration of $Zn^{\cdot\cdot}$ is 10^{37} times that of $Cu^{\cdot\cdot}$, or in other words, the solution pressure of zinc is 10^{37} times that of copper.

The relation between electromotive force and chemical equilibrium was thoroughly tested by Knüpffer* in the case of the reaction between thallium chloride and potassium thiocyanate, as represented by the equation

$$KSCN + TlCl \rightleftarrows KCl + TlSCN.$$

Since this reaction attains an equilibrium readily determinable by chemical analysis it is particularly well adapted to testing the electromotive force method for the determination of the equilibrium constant. The equilibrium represented by the above reaction not only exists at a definite temperature, but also undergoes a displacement in one direction or another as the temperature is changed, with a corresponding alteration in the concentrations of the potassium chloride and potassium thiocyanate solutions.

Knüpffer set up a cell involving the above substances according to the following scheme:

Thallium amalgam	KCl soln. sat'd with TlCl	KSCN soln. sat'd with TlSCN	Thallium amalgam.

Since the thallium chloride and the thallium thiocyanate are both present as solids, the concentrations of these substances may be

* Knüpffer, Zeit. phys. Chem., 26, 255 (1898).

regarded as remaining constant. According to equation (45), we may write

$$W = EF = RT \ln K - RT \ln \frac{c_{KCl}}{c_{KSCN}},$$

or

$$E = \frac{RT}{F} \ln K - \frac{RT}{F} \ln \frac{c_{KCl}}{c_{KSCN}} \qquad (47)$$

The electromotive force of the above cell was measured at 0.8° C., 20° C., and 39.9° C., and the corresponding values of the equilibrium constant, K, calculated. The respective values of K thus determined were as follows: 1.79, 1.26, and 0.88, while the values as found by direct analysis were, 1.74, 1.24 and 0.85. It thus appears that the electromotive force method may be relied upon for the accurate determination of equilibrium constants.

(8) *Oxidation and Reduction Elements.* When a dissolved substance passes from a lower to a higher state of oxidation, the change in the positive ion may be considered as due to an increase in the number of electrical charges on the ion. Thus, when a ferrous salt is oxidized to the ferric state, the change may be represented by the equation,

$$Fe^{\cdot\cdot} + (+) \rightarrow Fe^{\cdot\cdot\cdot},$$

or

$$Fe^{\cdot\cdot} \rightarrow Fe^{\cdot\cdot\cdot} + \ominus.$$

Similarly, the reduction of a ferric salt to the corresponding ferrous salt may be represented by the reverse equation,

$$Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot} + (+),$$

or

$$Fe^{\cdot\cdot\cdot} + \ominus \rightarrow Fe^{\cdot\cdot}.$$

The formation of zinc ions from metallic zinc may be considered as an oxidation, and may be represented by the equation,

$$Zn + 2(+) \rightarrow Zn^{\cdot\cdot},$$

or

$$Zn \rightarrow Zn^{\cdot\cdot} + 2\ominus.$$

The formation of negative ions from a non-metallic element may be considered as a reduction, as for example, the change of potas-

sium ferricyanide to potassium ferrocyanide, which may be represented by the equation,

$$Fe(CN)_6''' + (-) \rightarrow Fe(CN)_6'''',$$

or

$$Fe(CN)_6''' + \ominus \rightarrow Fe(CN)_6''''.$$

The foregoing considerations lead to the following definition of the terms, oxidation and reduction: *Oxidation is the process in which a substance takes up positive, or parts with negative charges, while reduction is the process in which a substance takes up negative, or parts with positive charges.*

According to this definition, oxidation always takes place at the anode and reduction at the cathode.

The oxidizing or reducing power of different electrolytes may readily be compared by measuring the resulting electromotive force, when the given substances are made the active agents in a cell. For example, if a platinum electrode be immersed in a solution containing both a ferrous and a ferric salt, and this, in turn, be connected with a calomel electrode as the other half-element, we will have a cell, the electromotive force of which will furnish a measure of the oxidation, or reduction, process occurring within it. The foregoing cell may be conveniently represented by the scheme,

$$(Hg) \begin{matrix} Hg_2Cl & Fe''' \\ Hg_2'' & Fe'' \end{matrix} (Pt).$$

If we assume that ferric ions are reduced to ferrous ions, the direction of the current within the cell will be from right to left, and the process may be represented by the equation,

$$2\,Fe''' + Hg_2 \rightarrow Hg_2'' + 2\,Fe''.$$

When equilibrium is reached, the equilibrium constant will be

$$K = \frac{c'_{Hg_2''} \times c'^{2}_{Fe''}}{c'^{2}_{Fe'''} \times c'_{Hg_2}}, \tag{48}$$

where c' denotes equilibrium concentration. But $c'_{Hg_2''}$ and c'_{Hg_2} are constant, hence we have

$$K' = \frac{c'^{2}_{Fe''}}{c'^{2}_{Fe'''}}, \tag{49}$$

and therefore,

$$W = RT \ln K' - RT \ln \frac{c_{Fe^{3\cdot\cdot}}}{c_{Fe^{2\cdot\cdot\cdot}}}. \tag{50}$$

Since the reaction represented by the above equation corresponds to the passage of two faradays of electricity, we have, remembering that $W = nEF$,

$$E = \frac{RT}{2F} \ln K' - \frac{RT}{2F} \ln \frac{c^2_{Fe^{\cdot\cdot}}}{c^2_{Fe^{\cdot\cdot\cdot}}}. \tag{51}$$

If we replace $\frac{RT}{2F} \ln K'$ by E_0, the preceding equation becomes,

$$E = E_0 - \frac{RT}{2F} \ln \frac{c^2_{Fe^{\cdot\cdot}}}{c^2_{Fe^{\cdot\cdot\cdot}}},$$

or

$$E = E_0 - \frac{RT}{F} \ln \frac{c_{Fe^{\cdot\cdot}}}{c_{Fe^{\cdot\cdot\cdot}}}. \tag{52}$$

The value of the electromotive force of the cell, when the concentrations of $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ are equal, is E_0, the latter being called the *normal potential* of the process.

If instead of the reduction reaction, we had considered the oxidation reaction,

$$2\,Fe^{\cdot\cdot} + Hg_2^{\cdot\cdot} \rightarrow 2\,Fe^{\cdot\cdot\cdot} + Hg_2,$$

we would have derived as the expression for the oxidation potential,

$$E = E_0 - \frac{RT}{F} \ln \frac{c_{Fe^{\cdot\cdot\cdot}}}{c_{Fe^{\cdot\cdot}}}. \tag{53}$$

(Let the student derive equation (53).)

All reversible oxidation and reduction processes are similarly related to each other, and the following equation gives the general relationship between ionic concentrations and the resulting electromotive force:

$$E_{(c_o \rightarrow c_i)} = E_0 - \frac{RT}{nF} \ln \frac{c_i}{c_o}, \tag{54}$$

where $E_{(c_o \rightarrow c_i)}$ is the electromotive force produced by the passage from the lower, or "ous" state of oxidation, to the higher, or "ic" state of oxidation; E_0 is the normal potential, c_o and c_i are the

ionic concentrations of the lower and higher states of oxidation, respectively, and n is the difference in valence of the two kinds of ions.

Equation (54) is sometimes referred to as "Peters' Equation," because of the fact that its applicability to various oxidation and reduction reactions was first demonstrated by Peters.*

Thus, Peters studied a ferri-ferro oxidation-reduction cell in which he prepared various mixtures of two stock solutions, the one consisting of N/10 ferrous chloride + N/10. hydrochloric acid, and the other of N/10 ferric chloride + N/10 hydrochloric acid. The hydrochloric acid was added to prevent hydrolysis. In order to measure the difference of potential of the ferri-ferro electrode, he set up a series of cells according to the following scheme in which the ratio of the concentrations of $Fe^{...}$ to $Fe^{..}$, expressed on a percentage basis, was systematically varied:

$$\begin{array}{l|l|l|l} +0.2822 & & +0.655 & \\ Hg - Hg_2Cl_2, NKCl & \text{Sat'd KCl} & 10\%\ Fe^{...} & \text{Pt} \\ & & 90\%\ Fe^{..} & \end{array}$$

$$E = E^+ - E^- = 0.655 - 0.282 = 0.373 \text{ volt.}$$

The results of Peters' measurements for an entire series of ferri-ferro cells is given in the following table.

FERRI-FERRO POTENTIALS

Ratio $Fe^{...} : Fe^{..}$ Per cent.	Obs. E.M.F. E.	Absolute P.D. $Fe^{...} - Fe^{..}$ Electrode.	Normal Oxidation Potential, N Cal. Electrode as Zero, E_0.	Equilibrium Constant $\frac{c'Fe^{..}}{c'Fe^{...}} = K$.
0.5 : 99.5	+0.298	+0.580	+0.430	
2 : 98	+0.333	+0.515	+0.430	
10 : 90	+0.373	+0.655	+0.428	
30 : 70	+0.408	+0.690	+0.429	Mean Value
40 : 60	+0.420	+0.702	+0.430	$10^{7.45}$
50 : 50	+0.431	+0.713	+0.431	
80 : 20	+0.465	+0.747	+0.430	
90 : 10	+0.480	+0.762	+0.425	

The values of E_0 are computed on the assumption that the ratio of the concentrations of the ferric and ferrous ions is identical with

* Peters, Zeit. phys. Chem., 26, 193 (1898).

the ratio of the concentrations of the respective salts, an assumption which is, of course, only approximately correct. The validity of the theory, however, is attested by the constancy of the values of E_0 as given in the fourth column of the table. The enormous average value of the equilibrium constant, K, shows that, when equilibrium is reached in the ferri-ferro solution, the ratio of the concentrations of ferrous to ferric ions is in the neighborhood of 10,000,000 : 1.

Since the tendency of hydrogen to pass into the ionic condition, when in contact with a normal solution of hydrogen ions, is zero, it follows that all oxidation potentials should be expressed in terms of the hydrogen electrode as standard. Hence, if the electromotive force of an oxidation element has been measured in conjunction with a calomel electrode, it should be converted to the hydrogen standard. Since the normal calomel electrode and the hydrogen electrode, when connected, give an electromotive force of 0.282 volt, it is evident that

$$E_H = E_C - 0.282,$$

where E_H denotes the potential of the hydrogen electrode and E_C the potential of the calomel electrode.

Although a large number of different oxidation cells have been studied by numerous investigators, much of the existing data on normal oxidation potentials is in need of careful revision. The reason for this lack of precision is largely due to the fact that liquid potentials have been only incompletely eliminated, and also because of the absence of reliable data on the activity of an electrolyte in the presence of one or more electrolytes. In general, it may be said that the published values of oxidation-reduction electrode potentials are to be regarded as close approximations only.

A few of the more reliable oxidation-reduction electrode potentials are given in the following table.

It has already been shown that the hydrogen electrode can be employed to determine end-points in neutralization reactions, and it now remains to point out that a modification of this method is applicable to the determination of the end-points in reactions involving oxidation and reduction. If a platinum electrode is introduced into the solution of an oxidizing agent, such as chromic acid, and the side-tube of a calomel electrode is also dipped into

OXIDATION-REDUCTION ELECTRODE POTENTIALS

Electrode.	Temp.	E_0 Volts. $H^+=H=0$.	Authority
Pt, $Co^{\cdots}$, $Co^{\cdot\cdot}$	25° C.	+1.817	Lamb and Larson*
Pt, $Mn^{\cdots\cdot}$, $Mn^{\cdots}$	12°	+1.642	Grube and Huberich†
Pt, $Mn^{\cdots\cdot}$, $Mn^{\cdot\cdot}$	12°	+1.577	" " "
Pt, $Mn^{\cdots}$, $Mn^{\cdot\cdot}$	12°	+1.511	" " "
Pt, $Fe^{\cdots}$, $Fe^{\cdot\cdot}$	25°	+0.747	Noyes and Brann‡
Hg, $Cr^{\cdots}$, $Cr^{\cdot\cdot}$	25°	+0.400	Forbes and Richter§
Hg, $Ti^{\cdots}$, $Ti^{\cdot\cdot}$	25°	+0.37	Forbes and Hall‖
Pt, $Ti^{\cdots\cdot}$, $Ti^{\cdots}$	18°	+0.056	Diethelm and Foerster¶
Hg, $Sn^{\cdots\cdot}$, $Sn^{\cdot\cdot}$ (+HCl)	25°	−0.426	Forbes and Bartlett**
Pt, $Sn^{\cdots\cdot}$, $Sn^{\cdot\cdot}$ (+NaOH)	18°	−0.854	Foerster and Dolch††

* Lamb and Larson, Jour. Am. Chem. Soc., **42**, 2024 (1921).
† Grube and Huberich, Zeit. Elektrochem. **29**, 8 (1923).
‡ Noyes and Brann, Jour. Am. Chem. Soc., **34**, 1016 (1912).
§ Forbes and Richter, Ibid., **39**, 1140 (1917).
‖ Forbes and Hall, Ibid., **46**, 385 (1924).
¶ Diethelm and Foerster, Zeit. phys. Chem., **62**, 129 (1908).
** Forbes and Bartlett, Jour. Am. Chem. Soc., **36**, 2030 (1910)
†† Foerster and Dolch, Zeit. Elektrochem., **16**, 590 (1910).
See also Gerke, Chem. Reviews, Vol. I, No. 4, p. 377.

the same solution, a cell having a definite electromotive force is formed. On adding to the chromic acid solution successive portions of a solution of a reducing agent, such as ferrous sulphate, a relatively small change in the electromotive force of the cell will be observed until the chromic acid is completely reduced. Then, on adding a single drop of the reducing agent, in excess of that required to reduce the chromic acid, a sudden drop in electromotive force will occur.

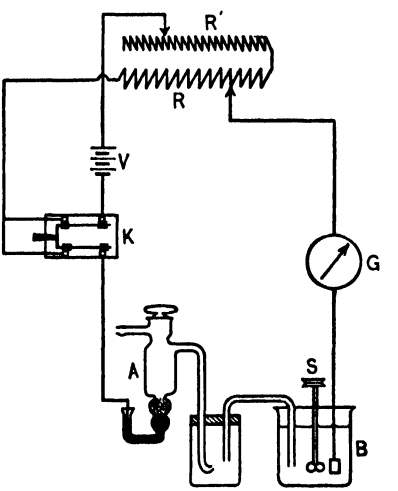


Fig. 154

A diagram of the apparatus, suitable for the above and similar electrometric titrations, is shown in Fig. 154. The solution to be titrated is introduced into the beaker, *B*, and a platinum electrode, *E*, and the side tube of a calomel electrode, *A*, are immersed in the solution. A gal-

vanometer, G, and two sliding resistances, R and R', are connected with the battery, V, and the titration cell through a double-pole switch, K. By means of the latter both the galvanometer and the cell may be thrown into the circuit in a single operation. The solution is stirred by means of a stirrer, S, driven by an electric motor while the titrating solution is delivered into the solution by means of a burette not shown in the sketch.

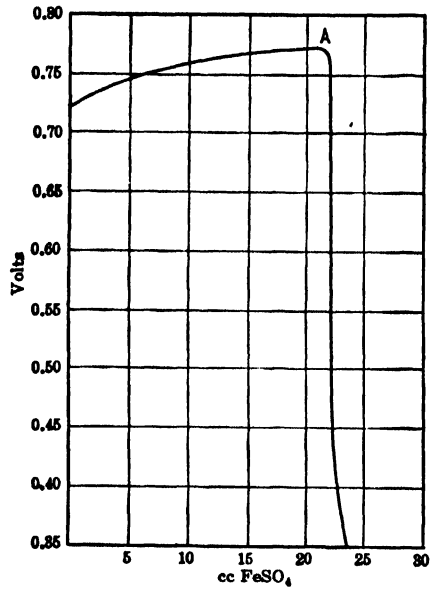


Fig. 155

The results of a typical titration with this apparatus are represented graphically in Fig. 155. In this experiment, 200 cc. of a solution of potassium bichromate were titrated with a solution of ferrous sulphate of equivalent strength, in the presence of sulphuric acid. It will be seen that the electromotive force rose very slowly from the initial value, 0.720 volt, to the point A, corresponding to 0.766 volt. When an excess of only 0.1 cc. of the ferrous sulphate solution was added, the electromotive force dropped 0.004 volt, while on adding a second 0.1 cc. portion, a drop of 0.313 volt occurred. This corresponds to the end-point of the reaction. Further addition of the reducing solution caused relatively little change in the value of the electromotive force.

This method of titrating chromates with ferrous sulphate was first used by Hildebrand* and, shortly afterward, by Forbes and Bartlett.† While working on the application of this method to the determination of chromium in steel, Kelley and Conant‡ found that it could be employed equally well in the determination of

* Hildebrand, Jour. Am. Chem. Soc., **35**, 869 (1913).
† Forbes and Bartlett, Ibid., **35**, 1527 (1913).
‡ Kelley and Conant, Ibid., **38**, 341 (1916).

vanadium and manganese in both steels and ferro-alloys. Subsequent investigations have demonstrated that this method is applicable to a large number of oxidation-reduction reactions.*

(9) *Ionization and Activity.* If in the equation for the electromotive force of a concentration cell, we substitute the observed value of E, and solve the equation for the ratio, c_2/c_1, we find that the value thus obtained does not agree with the value derived from conductance measurements. In other words, if m_1 and m_2 are the actual molal concentrations of the two solutions forming the cell, and α_1 and α_2 are the corresponding degrees of ionization, we find that the ratio, $m_2\alpha_2/m_1\alpha_1$, is not equal to the ratio, c_2/c_1, as calculated from the electromotive force of the cell. This is shown by the following table, which gives the ratios of the ionic concentrations of solutions of potassium chloride corresponding to various ten-to-one salt concentrations.

RATIOS OF ION CONCENTRATIONS IN SOLUTIONS OF POTASSIUM CHLORIDE

c_2/c_1 (Concentration Ratio.)	c_2/c_1 (Conductance).	c_2/c_1 (Electromotive Force).
0.5 : 0.05	8.85	8.09
0.1 : 0.01	9.16	8.33
0.05 : 0.005	9.30	8.64
0.01 : 0.001	9.62	9.04

The figures in the last column of the table are known as *activity ratios.*

The term "activity" may be defined as that quantity which, when substituted for the concentration of a given substance in the mass-action equation, will express its effect in determining

* Hendrixson, Jour. Am. Chem. Soc., **43**, 1309 (1921); Ibid., **45**, 2013 (1923); Hendrixson and Verbeck, Ibid., **44**, 2382 (1922); Kolthoff, Rec. Trav. Chim., **39**, 208 (1920); **40**, 532 (1921); **41**, 343 (1922); **42**, 186 (1922); Müller and Adam, Zeit. Elektrochem., **29**, 49 (1923); Müller and Gäbler, Zeit. anal. Chem., **62**, 29 (1923); Müller, Zeit. anorg. Chem., **125**, 125 (1923); Müller and Just, Ibid., **125**, 155 (1922); Müller and Wahle, Ibid., **129**, 33 (1923); Willard and Fenwick, Jour. Am. Chem. Soc., **45**, 645 (1923); **45**, 623 (1923); **45**, 84 (1923); **45**, 936 (1923); **45**, 928 (1923); **45**, 933 (1923); **45**, 715 (1923); van der Meulen and Wilcoxon, Ind. Eng. Chem., **15**, 62 (1923).

the equilibrium. In other words, the activity of a given substance is its "effective concentration."

It is customary to denote the activity of a solute by the symbol, a_2. If the solute is a uni-univalent electrolyte, such as KCl, the activities of the cation and anion may be represented by a^+ and a^-, respectively, and the equation for chemical equilibrium is then written in the form

$$\frac{a^+ \cdot a^-}{a_2} = K, \tag{55}$$

where K is a constant for any given temperature.

At infinite dilution, the activity of each of the ions of KCl is placed equal to its molal concentration, which, in the case where dissociation is complete, will be equal to the molal concentration of the solution. Since the concentration of the undissociated portion of strong electrolytes is not known with certainty, it is customary to let $K = 1$ in equation (55), and, thereby, define the activity of a solute, such as KCl, as the product of the activities of its two ions, thus,

$$a^+ \cdot a^- = a_2. \tag{56}$$

The *mean activity*, a, of the solute is then defined by the equation

$$a = (a^+ \cdot a^-)^{\frac{1}{2}}, \tag{57}$$

while the *activity coefficient*, γ, is defined as the mean activity product of the ions divided by the molal concentration of the electrolyte. The activity coefficient of a uni-univalent electrolyte will be, therefore,

$$\gamma = \frac{a}{c} = \left(\frac{a^+ \cdot a^-}{c^2}\right)^{\frac{1}{2}}, \tag{58}$$

or, the square root of the product of the activity coefficients of the ions.

The Nernst equation may now be written in the form

$$E = \frac{RT}{nF} \ln \frac{a_+'' \cdot a_-''}{a_+' \cdot a_-'}, \tag{59}$$

where the single and double accents denote the activities of the solute at two different concentrations.

Since $a = (a^+ \cdot a^-)^{\frac{1}{2}} = c\gamma$, it follows that equation (59) may be written in the form,

$$E = \frac{2\,RT}{nF} \ln \frac{c''\gamma''}{c'\gamma'}, \tag{60}$$

which, at 25° C., becomes, on passing to Briggsian logarithms,

$$E = 0.1183 \log \frac{c''\gamma''}{c'\gamma'}. \tag{61}$$

Now if the value of γ is known at one concentration, its value may be calculated at any other concentration, and if it be assumed that the activity coefficients of the ions at the lowest concentrations at which accurate measurements can be made are identical with the corresponding conductance ratios, it follows that the activity coefficients at other concentrations can be computed. In this manner the activity coefficients given in the following table have been determined.

ACTIVITY COEFFICIENTS AT 25° C.

c	KCl	KBr	NaCl	LiCl	KOH	HCl	H_2SO_4
0.001	0.961	0.961	0.963	0.965	0.965	0.984	.....
0.01	0.903	0.903	0.906	0.922	0.920	0.924	0.617
0.03	0.851	0.851	0.857	0.864	0.857	.....	.....
0.05	0.816	0.816	0.834	0.843	0.822	0.860	0.397
0.1	0.779	0.766	0.792	0.804	0.792	0.814	0.313
0.2	0.723	0.724	0.745	0.774	0.763	0.783	0.244
0.3	0.695	0.692	0.714	0.752	0.748	.....	0.209
0.5	0.659	0.653	0.682	0.754	0.740	0.762	0.178
1	0 613	0.597	0.652	0.776	0.775	0.823	0.150
2	0.566	0.580	0.672	0.936	.....	.....	0.147
3	0.575	0.630	0.722	1.20	1.136	1.35	0.166
4	.....	.....	0.794	.....	.....	.....	0.203
5	.....	.....	0.892	.....	.....	.....	0.242
6.12	.....	.....	1.019 (sat.)	.....	.....	.....	.....

It will be noticed that the activity coefficients of these electrolytes pass through a distinct minimum value but that the minima do not occur at the same concentration for each solute. The activity coefficients of three uni-univalent chlorides are plotted against their concentrations in Fig. 156; these curves not only reveal the presence of minima in the values of the activity co-

efficients, but also they show that the latter are greater in those solutions whose cations possess high hydration values.

The activity coefficients of a large number of electrolytes, both alone and mixed, in solutions of varying concentrations have been determined with a high degree of accuracy during recent years.*

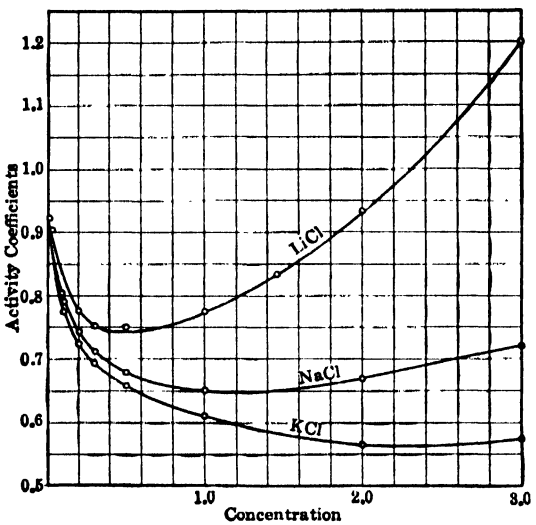


Fig. 156

Modern Theories of Ionization. Although the Ostwald dilution law has been found to hold for extremely dilute solutions of all

* MacInnes and Parker, Jour. Am. Chem. Soc., **37**, 1445 (1915); MacInnes and Beattie, Ibid. **42**, 1117 (1920); Beattie, Ibid. **42**, 118 (1920); Pearce and Hart, Ibid. **43**, 2483 (1921); Allmand and Polack, Jour. Chem. Soc., **115**, 1020 (1919); Ming Chow, Jour. Am. Chem. Soc., **42**, 488 (1920); Knobel, Ibid. **45**, 70 (1923); Getman, Ibid. **42**, 1556 (1920); Harned, Ibid. **37**, 2460 (1915); **42**, 1808 (1920); **44**, 252 (1922). Harned and Brumbaugh, Ibid. **44**, 2729 (1922); Horsch, Ibid. **41**, 1787 (1919); Lewis and Randall, Ibid. **43**, 1112 (1921); Linhart, Ibid. **39**, 615, 2601 (1917); **41**, 1775 (1919); Loomis, Essex and Meacham, Ibid. **39**, 1133 (1917); MacInnes, Ibid. **41**, 1086 (1919); Noyes and Ellis, Ibid. **39**, 2532 (1917); Noyes and MacInnes, Ibid. **42**, 239 (1920); Randall and Cushman, Ibid. **40**, 393 (1918); Lucasse, Ibid. **48**, 626 (1926); Pearce and Gelbach, Jour. Phys. Chem., **29**, 1023 (1925); Schreiner, Zeit. anorg. Chem., **121**, 321 (1922); McKeown, Trans. Faraday Soc., **17**, 517 (1922); Bjerrum, Zeit. anorg. Chem., **109**, 280 (1920); Zeit. phys. Chem., **104**, 406 (1923); Corran and Lewis, Jour. Am. Chem. Soc., **44**, 1673 (1922); Scatchard, Ibid. **47**, 641, 648 (1925); Harned, Ibid. **47**, 676, 684, 689 (1925).

electrolytes, whether weak or strong, its failure in the case of moderately concentrated solutions of strong electrolytes has led many investigators to abandon it entirely. Thus, Milner* rejected the idea that the degree of ionization of solutions of strong electrolytes is dependent upon their concentration, and accepted as a working hypothesis the view, earlier advanced by Sutherland,† that ionization in such solutions is practically complete. In terms of this theory the abnormalities of strong electrolytes are attributed to the influence of interionic forces. While the theory has much to commend it, there is as yet no more direct evidence in favor of the existence of completely dissociated molecules than there is for the existence of completely undissociated molecules.

The decrease in conductance which is observed when the concentration of the solution of a strong electrolyte is increased, Milner attributes to the diminished mobilities of the ions due to interionic forces. This same view has been put forward by Noyes and MacInnes,‡ who ascribe the observed variations in the conductance ratio, Λ/Λ_0, to changes in the mobilities of the ions rather than to changes in the number of ions. They further point out that the theory of interionic attraction offers a satisfactory explanation of the fact that numerous compounds are apparently dissociated to the same extent, although they may differ markedly in chemical character.

The theoretical investigation of the influence of interionic forces leads to the conclusion that a change in concentration will produce identical variations in the conductance and the osmotic pressure of the ions. The effect of the interionic forces is to cause an increase in the frequency with which the ions are apparently associated, resulting in a reduction of their osmotic pressure. In consequence of the reduction of the time during which the ions are actually free, the average mobility of the ions is diminished in the same ratio, and the established experimental facts pertaining to the osmotic pressure and the conductance of electrolytes can thus be satisfactorily explained.

Milner's theory is incomplete, in that it fails to offer any explanation as to why the law of mass action is applicable to solutions in which the solvent possesses a low dielectric constant.

* Milner, Phil. Mag., **35**, 214 (1918).

† Sutherland, Ibid. **3**, 161 (1902).

‡ Noyes and MacInnes, Jour. Am. Chem. Soc., **42**, 239 (1920).

Furthermore, no satisfactory expression has, as yet, been derived on the basis of this theory in which the conductance of a solution appears as a function of its concentration.

Another alternative to the Arrhenius theory of ionization, which has attracted wide attention, is that advanced by Ghosh.* Like Milner, Ghosh contends that the fundamental concept underlying the classical theory of Arrhenius fails to apply to strong electrolytes. According to his theory, the relations between the ions are governed by electrical forces, while the interior of the solution of an electrolyte is characterized by a certain potential which affords a measure of the work required to remove the ions from the influence of their mutual forces. From kinetic considerations, Ghosh concludes that the ions will become "free" when their velocity exceeds a certain limiting value.

The theory of Ghosh has been severely criticized by Kendall,† who not only points out the inconsistency of several of the fundamental postulates upon which the theory is based, but also directs attention to the fact that the rôle of the solvent in ionization is completely ignored. The theory has been further criticized by Partington,‡ and also by Chapman and George,§ the latter of whom contend that the formula developed by Ghosh for the calculation of the number of free ions is erroneous, and that when this expression is corrected the results obtained with it are not in agreement with existing experimental data. It is apparent, therefore, that although the Ghosh theory may be regarded as a rational attempt to account for the anomalies presented by solutions of strong electrolytes, it must be modified in several respects before it can be widely accepted.

A theory advanced by Debye and Hückel‖ gives promise of furnishing for the first time a satisfactory explanation of the deviations of highly dissociated substances from the laws of ideal solutions. While the development of this important theory is too highly mathematical for a text-book of this character, the simple assumptions upon which it is based should be stated. In

* Ghosh, Jour. Chem. Soc., 113, 449, 627, 707, 790 (1918); Zeit. phys. Chem., 98, 211 (1912).

† Kendall, Jour. Am. Chem. Soc., 44, 717 (1922).

‡ Partington, Trans. Faraday Soc., 15, 98 (1919).

§ Chapman and George, Phil. Mag., 41, 199 (1921).

‖ Debye and Hückel, Physik. Zeit., 24, 305 (1923).

addition to assuming complete dissociation of the solute, Debye and Hückel assume that the departure of electrolytes from the laws which express the behavior of ideal solutes in dilute solutions is to be ascribed to interionic electrical effects and not to chemical reactions between the ions. In consequence of the electrical attraction between the positive and negative ions, there will be, on an average, in the neighborhood of any one ion more ions of unlike than of like charges.

It follows, therefore, that when a dilute solution is further diluted, the separation of the ions will involve the performance of a certain amount of internal work against this electrical attraction with a corresponding increase in the energy content of the solution. Upon these two simple assumptions, Debye and Hückel derive an equation of the form,

$$1 - \phi = w \frac{\epsilon^2}{6\sqrt{KDT}} \sqrt{\frac{4\pi\epsilon^2}{KDT} n\nu} \qquad (62)$$

in which $\epsilon = 4.77 \times 10^{-10}$ electrostatic units; $D = 88.23$ when $T = 273$; and $k = 1.346 \times 10^{-16}$ ergs; $n =$ the number of ions in a cubic centimeter $= 6.06 \times 10^{20}\, c$, c being the molal concentration; and where $\phi = i/\nu$, ν being the number of ions formed by the dissociation of one molecule of solute and i, the van't Hoff factor. Equation (62), therefore, simplifies to

$$1 - \phi = 0.270\, w \sqrt{\nu c}, \qquad (63)$$

at 0° C.

This equation, which shows that $1 - \phi$ is proportional to $\sqrt{c}$ at high dilutions and at constant temperature and pressure, has been thoroughly tested and found to hold with great accuracy. The theory has been further investigated by A. A. Noyes* and others with satisfactory results.

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* Noyes, Jour. Am. Chem. Soc., 46, 1080, 1098 (1924); 47, 2122 (1925).

Thermodynamics and Chemistry. Macdougall. Chapter XVII.
Thermodynamics and Free Energy of Chemical Substances. Lewis and Randall. Chapters XXII, XXIII, XXV, XXVI, XXVII, XXIX, XXX.
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PROBLEMS

1. Calculate the heat of amalgamation of cadmium at 0° from the following data: — the electromotive force of a cell made up of a 1 per cent cadmium amalgam in a solution of cadmium sulphate is 0.06836 volt at 0°, and 0.0735 volt at 24°.45. *Ans.* 510 cal. per mol.

2. The electromotive force of the cell

$$\text{Pb} - 0.01\text{ m } \text{Pb(NO}_3\text{)}_2 - \text{sat. } \text{NH}_4\text{NO}_3 - \text{m KCl, } \text{Hg}_2\text{Cl}_2 - \text{Hg}$$

is −0.469 volt at 25°. The lead nitrate is 62 per cent ionized. What is the potential of lead against a solution containing 1 mol of Pb ions per liter, referred to the calomel electrodes as zero?

Ans. −0.405 volt.

3. Calculate the electromotive force of the cell

$$\text{Cu amalgam (a)} - \text{Solution } \text{CuSO}_4 - \text{Cu amalgam (b),}$$

at 20°.8, having given that the concentrations of the amalgams (a) and (b) are 0.0004472 and 0.00016645 respectively. *Ans.* 0.0167 volt.

4. Calculate the electromotive force of the cell

$$\text{Cu} - 0.01\text{ m } \text{CuSO}_4 - \text{m } \text{CuSO}_4 - \text{Cu,}$$

at 25°, having given the following values for the degree of ionization of the two solutions: — for m copper sulphate, $\alpha = 0.21$, and for 0.01 m copper sulphate, $\alpha = 0.61$. The electromotive force at the junction of the two solutions may be neglected. *Ans.* 0.0458 volt.

5. At 25° the electromotive force of the cell

$$\text{Zn} - 0.05\text{ m } \text{ZnSO}_4 - 0.5\text{ m } \text{ZnSO}_4 - \text{Zn}$$

is 0.018 volt. Neglecting the potential developed at the junction of the solutions, and assuming the dilute solution of zinc sulphate to be ionized to the extent of 35 per cent, find the degree of ionization of the concentrated solution. *Ans.* 0.142.

6. What is the electromotive force of the cell

$$\text{Zn} - 0.01\text{ m } \text{ZnSO}_4 - 0.1\text{ m } \text{ZnSO}_4 - \text{Zn,}$$

at 18°? For ZnSO_4, $\frac{v}{u+v} = 0.601$, for 0.1 molar ZnSO_4, $\alpha = 0.39$, and for 0.01 molar ZnSO_4, $\alpha = 0.63$. *Ans.* 0.027 volt.

7. The electromotive force of the cell

$$Ag - AgI, m\ KI - m\ KNO_3 - 0.001\ m\ AgNO_3 - Ag$$

is 0.72 volt at 18°. A molar solution of KI is 78 per cent ionized, and a 0.001 molar solution of $AgNO_3$ is 98 per cent ionized. Calculate the solubility of AgI. *Ans.* 1.72×10^{-8} mols per liter.

8. The potential of zinc against a solution containing one mol of Zn ions per liter is 0.493 volt, at 18°. Assuming complete dissociation, calculate the solution pressure of zinc in atmospheres.

9. The electromotive force of the Daniell cell

$$Zn - ZnSO_4 - CuSO_4 - Cu$$

is 1.0960 volt at 0°, and 1.0961 volt at 3°. Calculate the heat of the reaction taking place in the cell. 50,250 cal.

10. Calculate the electromotive force of the cell

$$Pt_{H_2} - 0.1\ m\ KOH - m\ HCl - Pt_{H_2},$$

at 25°, having given that 0.1 molar KOH is 85 per cent ionized and molar HCl is 70 per cent ionized. *Ans.* 0.757 volt.

11. The electromotive force of the cell

$$(Pt) \left| \begin{array}{l} 0.0337\ m\ Tl(NO_3)_3 \\ 0.0216\ m\ Tl(NO_3) \\ 0.42\ m\ HNO_3 \end{array} \right|$$

normal hydrogen electrode, is 1.2008 volts at 25°. On the assumption that the concentrations of the thallous and thallic ions are proportional to the concentrations of the corresponding nitrates, and regarding the potential of the hydrogen electrode as zero, calculate the normal potential of the thallic-thallous ion electrode. (The nitric acid is added to prevent hydrolysis of the thallic salt.)

12. The electromotive force of the cell

$$Hg - Hg_2Cl_2, m\ KCl \left| \begin{array}{l} 0.1\ m\ FeCl_3 \\ 0.1\ m\ FeCl_2 \\ 0.1\ m\ HCl \end{array} \right| (Pt)$$

is 0.375 volt at 25°. The normal potential of the ferric-ferrous electrode is 0.430, calculate the value of the ratio $c_{Fe^{+++}}/c_{Fe^{++}}$.

13. The electromotive force of the cell

$$Hg - Hg_2Cl_2 - 0.01\ m\ NaCl - 0.1\ m\ KCl - Hg_2Cl_2 - Hg$$

is 0.05403 volt at 25°, due allowance having been made for the junction potential. The electromotive force of the cell

$$Hg - Hg_2Cl_2 - 0.001\ m\ NaCl - 0.1\ m\ KCl - Hg_2Cl_2 - Hg$$

is 0.11200 volt at 25°, correction for the junction potential having been applied. Calculate the activity coefficient of 0.01 m NaCl. (Let the student look up the activity coefficient of 0.001 m NaCl in the table on p. 587.)

14. Calculate the electromotive force at 25° of the cell

$$K\ (amalgam) - 0.01\ m\ KCl,\ AgCl, -Ag - AgCl,\ 0.1\ m\ KCl - K\ (amalgam).$$

15. The temperature coefficient of the cell

$$Pb - PbCl_2,\ 0.1\ m\ KCl\ 0.1\ m\ KCl,\ Hg_2Cl_2 - Hg$$

is 0.00022 and its mean electromotive force at 20° is 0.5382 volt. Calculate the heat of the reaction

$$Pb + 2\ HgCl = PbCl_2 + 2\ Hg.$$

16. The electromotive force of the cell

$$H_2 - m/32\ C_6H_4NH_2.HCl - sat'd\ NH_4NO_3 - m\ KCl,\ Hg_2Cl_2 - Hg,$$

is 0.4655 volt at 25°, the current within the cell passing from left to right. Calculate the percentage hydrolysis of aniline hydrochloride.

17. The electromotive force of the cell

$$H_2 - solution\ CH_3COOH - m\ KCl,\ Hg_2Cl_2 - Hg$$

is 0.511 at 25°. Calculate the hydrogen ion concentration in the solution of acetic acid. Express the hydrogen ion concentration in terms of p_H.

18. A solution containing 50 cc. m/5 KH_2PO_4, 5.70 cc. m/5 NaOH and diluted to 200 cc. with pure water has been found to have a p_H value of 6.0. When a hydrogen electrode is immersed in this solution and connection is established with a normal calomel electrode, what electromotive force will result?

CHAPTER XVIII

ELECTROLYSIS AND POLARIZATION

Galvanic and Electrolytic Cells. The preceding chapter has been devoted to a consideration of galvanic, or voltaic cells, or cells in which chemical energy is transformed into electrical energy. We shall now consider very briefly the behavior of *electrolytic cells*, or cells in which electrical energy is consumed in effecting the decomposition of electrolytes. While the processes occurring within most of the galvanic cells treated in the preceding chapter are largely reversible, the processes occurring within electrolytic cells are almost wholly irreversible.

Current Density and Current Concentration. Two important factors involved in electrolytic processes are *current density* and *current concentration*. The ratio of the current strength in amperes to the area of the electrodes of an electrolytic cell, expressed in square decimeters, is known as the current density. The terms "cathodic" and "anodic" current density are employed to express the intensity of current per unit of area of the cathode or anode surface, respectively, in an electrolytic cell. The ratio of the current strength to the number of cubic centimeters of electrolyte is termed the "current concentration."

Current Efficiency. While theoretically 96,500 coulombs of electricity are required to separate one gram-equivalent of a substance in electrolysis, practically it is found that a greater quantity of electricity is required. This fact, however, does not imply a failure of Faraday's laws but rather is to be attributed to a number of causes among which may be mentioned the following: (1) Current leakage; (2) secondary reactions; and (3) loss of products of electrolysis. The ratio of the theoretical quantity of electricity to that actually required to effect the separation of a known weight of substance is termed the *current efficiency*. Current efficiency is a factor of great importance in all electrolytic processes.

Energy Efficiency. If it were possible to conduct an electrolytic process in a perfectly reversible manner and with a current

efficiency of 100 per cent, the quantity of electrical energy required would be equal to the product of the quantity of electricity used and the so-called "theoretical decomposition voltage." The actual, or working voltage, however, is always greater than the theoretical voltage, due to the fact that the electrode processes are not strictly reversible and also because of the resistance of the electrolyte. The ratio of the theoretical quantity of electrical energy to the quantity actually employed is known as the *energy efficiency*. The energy efficiency, like the current efficiency, of an electrolytic process is a factor of outstanding importance in all technical calculations involving electrolytic cells.

Polarization. If a difference of potential of about 1 volt is applied to two platinum electrodes, immersed in a concentrated solution of hydrochloric acid, it will be found that the current, which passes at first, will steadily diminish and ultimately will become zero. The cessation of the current has been shown to be due to the accumulation of hydrogen on the cathode and chlorine on the anode, these two gases setting up an opposing electromotive force, called the *electromotive force of polarization*. If the applied electromotive force be increased to 1.5 volts, the counter electromotive force will no longer be sufficient to reduce the current to zero. In fact, at any voltage above 1.35 volts a continuous current passes; this is termed the *decomposition potential* of hydrochloric acid.

At all voltages above the decomposition potential, the current, C, may be calculated by means of the formula,

$$E - e = CR, \tag{1}$$

where E is the applied electromotive force, e the counter electromotive force, and R the resistance of the electrolyte. As the applied electromotive force and the current increase, the polarization increases, since the gases are liberated under a pressure greater than that of the atmosphere. Since, however, the gases escape from the solution, the value of e can never become equal to E.

The decomposition potential of an electrolyte can be determined in either of two different ways: (1) by gradually raising the applied electromotive force, E, until it exceeds e, when the current will suddenly increase; or (2) by charging the electrodes

up to atmospheric pressure by means of an electromotive force greater than e, and after breaking the external circuit, measuring the counter electromotive force.

The arrangement of apparatus for the measurement of the electromotive force of polarization, as suggested by Le Blanc,* is indicated in Fig. 157. A is the electrolytic cell in which polarization occurs, B is the source of external electromotive force, C is a capillary electrometer, D is a source of variable potential, and E is one prong of an electrically-driven tuning fork which serves to make and break contact in rapid alternation with the points, F and G. When the tuning fork makes contact at F, the current flows through A, polarizing the electrodes; when contact is made at G, the counter electromotive force, due to polarization, causes a current to flow through D and C. The counter electromotive force is balanced by varying D, until no current flows through C. The potential of D is then equal to the electromotive force of polarization.

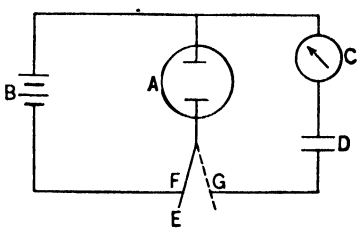

Fig. 157

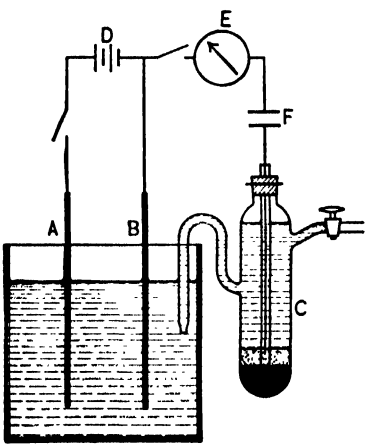

Fig. 158

Just as the electromotive force of a galvanic cell is due to the combined action of several differences of potential, so also the electromotive force of polarization is due to the individual differences of potential located at the electrodes. The method employed for the measurement of polarization at a single electrode was devised by Fuchs, and is illustrated diagrammatically in Fig. 158. The two electrodes, A and B, and the side tube of the normal calomel electrode, C, are immersed in the vessel containing the electrolyte. D is the source of external electromotive force, E is a capillary electrometer, and F is a source

* Zeit. phys. Chem., 5, 469 (1890).

of variable potential. Before closing the external circuit, *DAB*, the potential of the electrode, *B*, against the solution is measured. Then the circuit, *DAB*, is closed, thereby polarizing the electrode *B*. The external circuit is now broken, and the potential of *B* against the solution remeasured. The difference between the final and initial values of the electrode potential gives the value of the polarization at *B*. In like manner, the polarization at the other electrode can be measured.

The small amount of electricity which is necessary to polarize an electrode is termed the *polarization capacity of the electrode.* This factor is dependent upon the extent of surface of the electrode, and also upon the nature of the metal of which it is formed. The polarization capacity of palladium is greater than that of platinum, for electrodes of equal surface, when hydrogen is liberated on each. Palladium dissolves hydrogen more readily than platinum, and consequently a larger amount of hydrogen, and a correspondingly greater quantity of electricity will be required to bring the hydrogen dissolved in the palladium up to the same pressure as that of the hydrogen dissolved in the platinum. If, through the processes of solution or diffusion, or through chemical action, the substance which causes the polarization is removed, the electrode is said to be *depolarized.* Thus, when a reducing agent, such as ferrous chloride, is electrolyzed, the oxygen liberated at the anode immediately combines with the electrolyte, forming ferric chloride, and preventing polarization of the electrode.

If water be electrolyzed between platinum electrodes, the cathode becomes saturated with hydrogen, and the anode with oxygen, until, when the electromotive force of polarization becomes equal to that of the external circuit, the current ceases. The two gases, hydrogen and oxygen, are soluble, however, and consequently diffuse away from the electrodes, either escaping from the solution, or recombining to form water. In order to compensate for this continuous loss of gas at the electrodes, a small current continues to flow, thus maintaining the initial electromotive force constant. This small current is termed the *residual current.* If oxygen is bubbled over the surface of the cathode during electrolysis, the hydrogen is removed as rapidly as it is liberated. Such an electrode, on which no new substance is formed during electrolysis, is called an *unpolarizable electrode.*

Decomposition Potentials. The decomposition potential of an electrolyte can be determined, as has already been pointed out, by immersing two platinum electrodes in the solution and connecting with a source of electricity, the electromotive force of which can be varied at will. The voltage is gradually increased and the corresponding current is observed. It is found that the current increases at first, and then drops almost to zero every time the voltage is raised, until the decomposition potential is ultimately reached. Beyond this point the current has been found to be directly proportional to the electromotive force. If the applied electromotive forces are plotted as abscissæ, and the corresponding currents as ordinates, we obtain curves of the form shown in Fig. 159. Some of the decomposition potentials of molar solutions, as determined by Le Blanc,* are given in the accompanying tables.

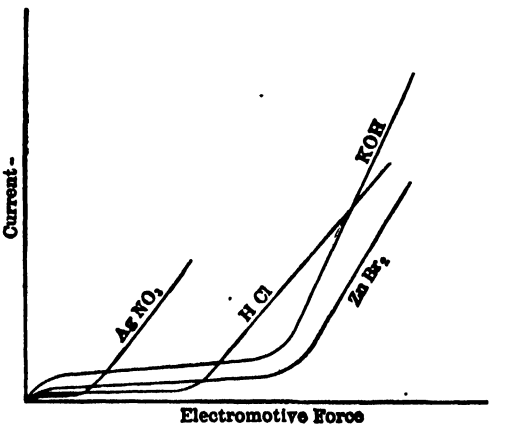

Fig. 159

DECOMPOSITION POTENTIALS

SALTS

Salt.	Decomp. Potential.	Salt.	Decomp. Potential.
	Volts.		Volts.
$ZnSO_4$	2.35	$Cd(NO_3)_2$	1.98
$ZnBr_2$	1.80	$CdSO_4$	2.03
$NiSO_4$	2.09	$CdCl_2$	1.88
$NiCl_2$	1.85	$CoSO_4$	1.92
$Pb(NO_3)_2$	1.52	$CoCl_2$	1.78
$AgNO_3$	0.70		

* Zeit. phys. Chem., 8, 299 (1891).

ACIDS

Acid.	Decomp. Potential.
	Volts.
H_2SO_4	1.67
HNO_3	1.69
H_3PO_4	1.70
$CH_2Cl.COOH$	1.72
$CHCl_2.COOH$	1.66
$CH_2(COOH)_2$	1.69
$HClO_4$	1 65
HCl	1.31
$(COOH)_2$	0.95
HBr	0.94
HI	0 52

BASES

Base.	Decomp. Potential.
	Volts.
NaOH	1.69
KOH	1.67
NH_4OH	1.74

It will be observed, that while there is considerable variation in the decomposition potentials of salts, there is very little variation in the decomposition potentials of acids and bases. There is a maximum value of about 1.70 volts to which many acids and bases closely approximate. It is found that all acids and bases, which decompose at 1.70 volts, give off hydrogen and oxygen at the electrodes. Those acids and bases which decompose at potentials less than the maximum, do not liberate hydrogen and oxygen. When their solutions are sufficiently diluted, however, hydrogen and oxygen are evolved, and the decomposition potential rises to the maximum value. Thus, Le Blanc found the following values for the decomposition potential of different dilutions of hydrochloric acid.

DECOMPOSITION POTENTIALS OF HCl

Concentration.	Decomp. Potential.
	Volts.
2 m HCl	1.26
$\frac{1}{2}$ m HCl	1.34
$\frac{1}{8}$ m HCl	1.41
$\frac{1}{32}$ m HCl	1.62
$\frac{1}{128}$ m HCl	1.69

When 2 m hydrochloric acid is electrolyzed, hydrogen and chlorine are given off at the electrodes, whereas, when the concentration of the acid is reduced to 1/32 m, hydrogen and oxygen are the products of electrolysis, and the decomposition potential increases to 1.70 volts. It is found that the values of the decomposition potentials vary slightly with the nature of the electrodes. The above values refer to platinum electrodes.

The Theory of Polarization. Our knowledge of the processes taking place at the electrodes, during electrolysis, is largely due to the investigations of Le Blanc. He determined the electromotive force of polarization at each electrode, varying the external electromotive force from zero up to the decomposition potential of the solution. When the decomposition value was reached, the potential of the electrode against the solution was found to be the same as the difference of potential between the solution and the element liberated at the electrode. Thus, the decomposition potential of a molar solution of zinc sulphate was found to be 2.35 volts, while the corresponding difference of potential between the electrode and the solution was found to be 0.493 volt. If a piece of pure zinc is immersed in a molar solution of zinc sulphate, the difference of potential will be found to be 0.493 volt, the metal being negative to the solution. It frequently happens that, before the decomposition point of the solution is reached, the electrode exhibits the potential of the deposited metal. For example, in a molar solution of silver nitrate, the electrode acquires the potential of pure silver in molar silver nitrate, before the decomposition value, 0.70 volt, is reached. This is due to the fact, that the osmotic pressure of the silver ions exceeds the solution pressure of the metal, resulting in the deposition of the ions of the metal without the application of any external electromotive force.

When an indifferent electrode, such as platinum, is immersed in a solution of a salt, a very small amount of ionic deposition must occur, otherwise, according to the Nernst equation, an infinite electromotive force must be established. Thus, in the equation,

$$E = \frac{RT'}{nF} \ln \frac{p}{P}, \tag{2}$$

if the solution pressure $P = 0$, it is evident, that $E = \infty$, and a perpetual motion must result. We are thus forced to the conclusion, that when an indifferent electrode is immersed in a salt

solution, ions will continue to separate upon it until the tendency for the deposited metal to go back into solution exactly counterbalances the tendency to separation. Hence, the electrode will become positive toward the solution. The magnitude of this difference of potential will be dependent upon the amount of metal deposited. It is to be noted that this difference of potential need not be equal to that between the massive metal and the solution. If the electrodes be connected with an external source of electromotive force, the value of which can be varied at will, and a small electromotive force be applied, more metal will separate on the cathode. This will cause an increase in the solution pressure P, tending to offset further deposition. A still further increase in the external electromotive force will cause the deposition of more metal and, as a result of the corresponding increase in P, further deposition at that voltage will be prevented. Ultimately, when the applied electromotive force is such that P acquires its maximum value, equivalent to that of the massive metal, continuous deposition will occur. An exactly analogous process takes place at the anode. If a gas is liberated, its concentration steadily increases until the maximum pressure is reached, when it will escape from the solution. When strong currents are employed, P does not remain constant, as has been assumed above, but gradually diminishes, causing the difference of potential at the electrode to increase. From the above considerations it becomes clear that a continuous decomposition of an electrolyte will take place only when the concentrations of the substances separating at the electrodes have attained their maximum values. When the decomposition point is reached, the electrode exhibits the potential characteristic of the massive metal. It is evident from the behavior of silver nitrate, and the salts of other metals, for which $p > P$, that the maximum values of concentration at the electrodes need not necessarily be attained simultaneously.

When the products of electrolysis are gaseous, the value of the decomposition potential depends upon the nature of the electrodes. Thus, the cell,

$$Pt_{H_2} - m\ H_2SO_4 - Pt_{O_2}$$

gives an electromotive force of 1.07 volts, if platinized platinum electrodes are used. If an external electromotive force slightly

greater than 1.07 volts be applied to this cell, in the reverse direction, a continuous decomposition of water will take place, and hydrogen and oxygen will be evolved at the electrodes. If on the other hand, the platinized electrodes are replaced by electrodes of polished platinum, the decomposition potential will be found to rise to 1.68 volts. The reverse electromotive force of polarization, however, is found to be only 1.07 volts. That is, the liberation of gas at a polished platinum electrode is an irreversible process. The difference in the behavior of the two electrodes is explicable when it is remembered, that platinum is capable of occluding large amounts of gas. A platinized electrode absorbs the liberated gas very slowly, and when thoroughly saturated, if it is not entirely immersed in the solution, it gradually gives up the gas by diffusion, no bubbles being formed. Thus, if the external electromotive force be raised to 1.07 volts, the system will be in equilibrium, while if the applied electromotive force be greater, or less, than the equilibrium value, a current will flow in one direction, or the other, gas being either liberated or dissolved. In other words, the cell is completely reversible.

Where polished platinum or gold electrodes are used, however, the decomposition potential is, as has been stated, 1.68 volts. Polished electrodes have relatively small absorbing power. Hence, if an electromotive force between 1.07 and 1.68 volts be applied, the gases cannot diffuse away from the electrode rapidly enough, and, when the solution in the vicinity of the electrodes becomes saturated with gas, the current will cease flowing. A very slow process of diffusion from the solution into the air is constantly taking place, however, and this permits the continuous evolution of an exceedingly small amount of gas, while a correspondingly small current traverses the solution.

In order to produce a steady electrolysis, it is necessary to raise the external electromotive force to such an intensity that bubbles are formed continuously at the surface of the electrodes. This calls for the performance of work, the amount of which is dependent upon the condition of the electrode surfaces, the surface tension of the solution, and various other factors. In cases where bubbles are formed, a portion of the available energy of the chemical process is not expended in effecting electrical separation; consequently, the reverse electromotive force is less than the applied, and the system is irreversible.

Passivity. It has long been known that if a piece of iron is momentarily immersed in concentrated nitric acid and then thoroughly rinsed in water, it not only becomes insoluble in acid but also fails to precipitate copper from solutions of its salts. This peculiar phenomenon is known as *passivity*, and the metal is said to be in the *passive state*. Other metals, such as chromium and nickel, also exhibit the phenomenon of passivity. Many metals acquire the property of passivity on being made the anode in an electrolytic cell. When in the passive state, the metals resemble the so-called "noble metals" in their behavior, and if they dissolve at all when functioning as the anode in a cell, the amount entering the solution is found not to correspond with that required by Faraday's law. For example, both chromium and manganese, when in the passive state, exhibit in solution a higher valence than when in the ordinary, or active state. Normally, chromium should dissolve as the $Cr^{\cdot\cdot}$ ion, but when it is made the anode in an alkaline electrolyte, it does not dissolve until the potential attains a value of approximately +0.34 volt. It then enters the solution as hexavalent $Cr^{\cdot\cdot\cdot\cdot\cdot\cdot}$ ions, which immediately react with the hydroxyl ions to form chromate ions according to the reaction,

$$Cr^{\cdot\cdot\cdot\cdot\cdot\cdot} + 8\,OH' = CrO_4'' + 4\,H_2O.$$

As a general rule, however, as the anodic current-density is increased, the proportion of the current carried by the ions of the metal entering the solution diminishes, the anions are discharged, and ultimately the metal entirely ceases to dissolve. Under these conditions the function of the current is merely to discharge the anions. The higher the current-density, the greater the passivity becomes. It is evident, therefore, that an intimate connection exists between passivity and polarization.

The subject of passivity has engaged the attention of chemists for many years, and numerous ingenious theories have been advanced in explanation of the phenomenon. These theories have been compiled and critically reviewed by Byers* and also by Bennett and Burnham.† Thus, Faraday,‡ in 1836, concluded that the cause of passivity was the formation of a thin protective

* Byers, Jour. Am. Chem. Soc., **30**, 1718 (1908).

† Bennett and Burnham, Trans. Am. Electrochem. Soc., **29**, 217 (1916).

‡ Faraday, Exp. Researches, Vol. II, p. 231.

film of oxide over the surface of the metal, while Le Blanc,* as the result of an extensive series of experiments, was led to regard the passive state as due to a change in the velocity of ionization of the metal.

Shortly after Le Blanc's investigations were completed, Fredenhagen† advanced the view that the passive state is to be attributed to change in the velocity of reaction between the metal and anodic oxygen. Bennett and Burnham,‡ however, have reached the conclusion that none of the above proposed explanations are tenable and suggest, instead, that passivity is probably due, in all cases, to the formation of an adsorbed oxide film on the surface of the metal which acts as a protective layer. According to this view, passivity should be developed by oxidizing conditions and prevented by reducing conditions. Quite recently, Smits§ has advanced another explanation of the phenomenon based upon his new theory of allotropy.

Overvoltage. The reactions occurring at the electrodes of an electrolytic cell are catalytically accelerated by the metal of which the electrodes are formed. Thus, platinized platinum is the most effective catalyst for the reaction represented by the equation,

$$H_2 + 2\,(+) \rightleftarrows 2\,H^{\cdot}.$$

Hydrogen is liberated on platinized platinum at 0 volt, on polished platinum at 0.09 volt, and on zinc at 0.70 volt. The electromotive force necessary to overcome the resistance of the chemical reaction at an electrode is termed *overvoltage*. Thus, we say that hydrogen is liberated on polished platinum with an overvoltage of 0.09 volt, and on zinc with an overvoltage of 0.70 volt. The following table gives the overvoltage necessary for the liberation of hydrogen and oxygen on electrodes of different metals.

Various theories as to the cause of overvoltage have been advanced. As the result of a rather extensive experimental investigation, Newberry|| concludes that overvoltage is determined by three different factors, namely: (1) Supersaturation of the elec-

* Le Blanc, Zeit. Elektrochem., 6, 472 (1900); 11, 9 (1905).
† Fredenhagen, Zeit. phys. Chem., 43, 1 (1903); 63, 1 (1908).
‡ loc. cit.
§ Smits, "Theorie der Allotropie," p. 424.
|| Jour. Chem. Soc., 105, 2419 (1914).

ELECTRODE OVERVOLTAGES

Hydrogen Liberation.		Oxygen Liberation.	
Metal.	Overvoltage.	Metal.	Overvoltage.
Pt (platinized)	0.00	Au	1.75
Au	0.01	Pt (polished)	1.67
Fe (in NaOH)	0.08	Pd	1.65
Pt (polished)	0.09	Cd	1.65
Ag	0.15	Ag	1.63
Ni	0.21	Pb	1.53
Cu	0.23	Cu	1.48
Pd	0.46	Fe	1.47
Sn	0.53	Pt (platinized)	1.47
Pb	0.64	Co	1.36
Zn	0.70	Ni (polished)	1.35
Hg	0.78	Ni (spongy)	1.28

trode surface with non-electrified gas under very high pressure, due to the permeability of the metal to the ionized gas; (2) deficiency or excess of non-hydrated ions in the immediate neighborhood of the electrodes; (3) inductive action of the escaping ionized gas on the electrode.

A general theory of overvoltage has been developed by Bennett and Thompson.* According to their theory, the excess of back electromotive force over the reversible electromotive force, is due to the accumulation, during electrolysis, of unstable products above the equilibrium concentration. Among such products are active hydrogen, H_1, active oxygen, O_1 and M_1, atomic metal, analogous to vaporized metal, in the case of metal overvoltages. These products are shown to be more reactive than the final products, and are sufficiently active to explain the overvoltages found experimentally. The authors claim for their theory that it offers an entirely satisfactory explanation of the known facts concerning overvoltage.

MacInnes and Adler,† as a result of their experimental studies on hydrogen overvoltage, conclude that it is due primarily to a layer of supersaturated, dissolved hydrogen in the electrolyte surrounding an electrode. If the electrode is capable of adsorbing sufficient hydrogen to form nuclei for bubbles of gas, the super-

* Jour. Phys. Chem., 20, 296 (1916).

† Jour. Am. Chem. Soc., 41, 194 (1919).

saturation cannot rise to high values, and the electrode will have a low overvoltage. On the other hand, metals possessing small adsorptive powers exhibit high overvoltages. The authors claim to have furnished experimental evidence in support of their theory.

Primary Decomposition of Water in Electrolysis. The decomposition potential of an electrolyte giving off hydrogen and oxygen at the electrodes, is dependent upon the concentrations of the two ions, $H^{\cdot}$ and OH', and is independent of the nature of the electrolyte. As has already been stated, the decomposition potential of all acids and bases, which give off hydrogen and oxygen, approximates to 1.70 volts. According to the law of mass action, the product of the concentrations of the $H^{\cdot}$ and OH' ions is constant, and independent of the other substances which may be present. Excluding solutions of salts which undergo reduction by hydrogen, and solutions of chlorides, bromides, and iodides oxidizable by oxygen, the ions $H^{\cdot}$ and OH', according to Le Blanc, are to be regarded as the sole factors in the electrolysis of solutions, and not the ions of the dissolved electrolyte. In other words, *electrolysis involves a primary decomposition of water.*

The electrical conductance of the solution is due to the ions of the electrolyte together with the ions of water, but at the electrode that process takes place which involves the expenditure of the minimum amount of energy, and this is, under ordinary conditions, the separation of the $H^{\cdot}$ and OH' ions. Thus, when a solution of potassium sulphate is electrolyzed by a current of moderate strength, it is not rational to assume that the $K^{\cdot}$ and SO_4'' ions are primarily discharged at the electrodes, and that these subsequently react with water. This may be made clear by considering the process taking place at the cathode. According to the explanation based upon so-called "secondary action," the $K^{\cdot}$ ions give up their positive charges to the electrode, and then react with water as indicated by the equation,

$$K + H^{\cdot} + OH' \rightarrow K^{\cdot} + OH' + H.$$

This explanation involves the transfer to the potassium atom of the positive charge of the $H^{\cdot}$ ion of water; this can only take place if the $H^{\cdot}$ ion holds its charge less tenaciously than the $K^{\cdot}$ ion. Hence, if the $H^{\cdot}$ ion parts with its charge more readily than the $K^{\cdot}$ ion, the former will be discharged primarily at the cathode.

Similar reasoning may be employed to explain the action at the anode. Therefore, in electrolysis all of the ions participate in conducting the current and collect around the electrodes, but since the $H^{\cdot}$ and OH' ions separate more easily, these are discharged primarily. With stronger currents it is possible to cause the separation of the $K^{\cdot}$ and SO_4'' ions also, since the number of $H^{\cdot}$ and OH' ions present is too small to carry all of the current, and the energy required to discharge the ions of the electrolyte is less than that necessary to remove the small number of residual $H^{\cdot}$ and OH' ions. The formation and decomposition of water are reversible processes, so that no loss of energy is involved, as would be the case if secondary actions occurred.

Electrolytic Separation of the Metals. Freudenberg* was the first to recognize the possibility of effecting the quantitative separation of different metals by means of graded electromotive forces. He showed that it was only necessary to select a salt of each metal, whose respective decomposition potentials differ as widely as possible, and electrolyze at an electromotive force intermediate between these potentials. The salt having the lower decomposition potential will decompose first, and when the deposition of the metal is complete, the current will practically cease flowing; then if the applied electromotive force be raised above the decomposition potential of the second salt, the second metal will be deposited. In practice it is found necessary to increase the applied electromotive force slightly, because of the gradual decrease in the number of ions of the salt having the lower decomposition potential. The amount of this increase may be readily calculated from the familiar equation,

$$E = \frac{RT}{nF} \ln \frac{p}{P}. \tag{3}$$

For example, suppose a mixture of the nitrates of cadmium, lead and silver is subjected to electrolysis, the decomposition potentials of the salts being as follows: — $Cd(NO_3)_2 = 1.98$ volts, $Pb(NO_3)_2 = 1.52$ volts, and $AgNO_3 = 0.70$ volt. If the applied electromotive force is made a little less than 1 volt all of the silver will be deposited; then if the electromotive force is raised to about 1.6 volts, all of the lead will be deposited; and finally, if the electromotive force be raised to about 2 volts the cadmium will be deposited.

* Zeit. phys. Chem., 12, 97 (1893).

In the subjoined table are given the separation potentials of some of the ions, the separation potential of the $H^{\cdot}$ ion being assumed to be equal to zero.

SEPARATION VALUES OF IONS FOR MOLAR CONCENTRATION

Ion.	Separation Potential.	Ion.	Separation Potential
$Ag^{\cdot}$	+0.78	I'	+0.52
$Cu^{\cdot\cdot}$	+0.34	Br'	+0.94
$H^{\cdot}$	−0.0	O''	+1.08 (in acid)
$Pb^{\cdot\cdot}$	−0.17	Cl'	+1.31
$Cd^{\cdot\cdot}$	−0.38	OH'	+1.68 (in acid)
$Zn^{\cdot\cdot}$	−0.74	OH'	+0.88 (in base)
		SO_4''	+1.9

According to this table the decomposition potential of water is equal to the sum of the separation potentials of its ions, or 1.68 volts.

Storage Cells or Accumulators. Storage cells or accumulators, as the name implies, are devices for the storage of electrical energy in the form of chemical energy. Any reversible cell may be employed as an accumulator. Thus, the oxygen-hydrogen cell,

$$Pt_{O_2} - \text{Solution of Sulphuric Acid} - Pt_{H_2},$$

may be used as an accumulator, if the gases resulting from the electrolysis of water are collected at the electrodes, and then used to produce a current. Practically, however, only two types of such secondary cells are in use to-day. These are, the almost universally used lead accumulator, and the less efficient nickel-iron accumulator.

If two lead plates are immersed in a 20 per cent solution of sulphuric acid, a minute amount of lead sulphate will be formed on the surface of each plate. If now a current of electricity is passed through the solution, the lead sulphate on the cathode will undergo reduction to metallic lead, and the lead sulphate on the anode will be oxidized to lead peroxide. In this manner we form the cell,

$$Pb - \text{20 per cent Sol. } H_2SO_4 - PbO_2.$$

The electromotive force of this cell is about 2 volts. The amounts of lead and lead peroxide produced in this way are so small that the cell can furnish only a very small amount of electrical energy. In order to increase its capacity, the electrodes should be given as large an amount of surface as possible. This may be brought about by the method of Planté, in which a solution of sulphuric acid is electrolyzed, first in one direction and then in the other, thus causing the plates to become spongy; or by the method of Faure, in which a lead "grid" charged with a paste of lead oxide and red lead, is introduced into a similar solution, and a current passed until spongy lead is formed at the cathode and lead peroxide is formed at the anode. If the charging circuit is then broken and the two electrodes are connected by a wire, a current will flow from the peroxide plate to the lead plate, while lead sulphate is slowly formed at each.

According to Le Blanc the following reactions take place during the discharge of the lead accumulator:

Positive Electrode.

(a) PbO_2 (solid) $\rightarrow$ PbO_2 (dissolved) $\rightarrow$ $Pb^{\cdots\cdot} + 2\ O''$.
(b) $4\ H^{\cdot} + 2\ O'' \rightarrow 2\ H_2O$.
(c) $Pb^{\cdots\cdot} + 2 \ominus \rightarrow Pb^{\cdot\cdot}$.
(d) $Pb^{\cdot\cdot} + SO_4'' \rightarrow PbSO_4$ (dissolved) $\rightarrow$ $PbSO_4$ (solid).

The total reaction at the positive electrode is, therefore,

$$PbO_2 + 4\ H^{\cdot} + SO_4'' + 2 \ominus \rightarrow PbSO_4 + 2\ H_2O.$$

Negative Electrode.

(a) $Pb \rightarrow Pb^{\cdot\cdot} + 2 \ominus$.
(b) $Pb^{\cdot\cdot} + SO_4'' \rightarrow PbSO_4$ (dissolved) $\rightarrow$ $PbSO_4$ (solid).

Hence the total reaction at the negative electrode is

$$Pb + SO_4'' \rightarrow PbSO_4 + 2 \ominus.$$

On combining the two preceding equations, we have, as the equation for the reaction of the cell as a whole,

$$PbO_2 + Pb + 2\ H_2SO_4 \rightarrow 2\ PbSO_4 + 2\ H_2O.$$

Since on charging the lead accumulator, the foregoing reactions take place in the reverse direction, it follows that the reactions

corresponding to both processes may be represented by a single equation, thus

$$PbO_2 + Pb + 2\,H_2SO_4 \underset{\text{(charge)}}{\overset{\text{(discharge)}}{\rightleftarrows}} 2\,PbSO_4 + 2\,H_2O.$$

At room temperature, the positive electrode potential of the lead accumulator will be, according to Nernst's equation,

$$E^+ = E_{0Pb^{++++}\to Pb^{++}} + \frac{0.059}{2}\log\frac{c_{Pb^{++++}}}{c_{Pb^{++}}},$$

while, in like manner, the negative electrode potential will be

$$E^- = E_{0Pb^{++}\to Pb} + \frac{0.059}{2}\log c_{Pb^{++}}.$$

It follows, therefore, that the total electromotive force of the cell must be

$$E = E^+ - E^- = E_{0Pb^{++++}\to Pb^{++}} - E_{0Pb^{++}\to Pb} + 0.029\log\frac{c_{Pb^{++++}}}{[c_{Pb^{++}}]^2}.$$

On substituting in the preceding equation the values employed by Cumming,* we have

$$E = 1.8 + 0.12 + 0.029\log\frac{0.91\times 10^{-4}}{(5\times 10^{-6})^2},$$

$$= 2.11 \text{ volts.}$$

This result is in satisfactory agreement with the commonly accepted experimental value of the normal initial voltage of the lead accumulator, viz., 2.05 volts.

A typical pair of charge and discharge curves for the lead accumulator are shown in Fig. 160. The ampere-hour efficiency of the lead cell is approximately 95 per cent, while the watt-hour, or energy efficiency, which is dependent upon the rate of charge and discharge, ranges from 75 to 85 per cent.

Since lead accumulators have come into such general use, it may not be amiss to include in this section a few directions as to their care and maintenance.

It is important that an accumulator should never be discharged below 1.80 volts. Cells should never be permitted to remain discharged, but as soon as the voltage drops to 1.80 volts they

* Cumming, Zeit. Elektrochem., 13, 19 (1907).

should be immediately recharged. When allowed to stand in a discharged condition for any length of time, "sulphating" occurs, i.e., hard crystals of lead sulphate are formed on the plates, thereby rendering subsequent attempts to recharge the cell exceedingly difficult. In charging, care must be taken to employ only direct current, and to connect the positive wire with the positive terminal of the cell. The rate at which cells should be charged is also of im-

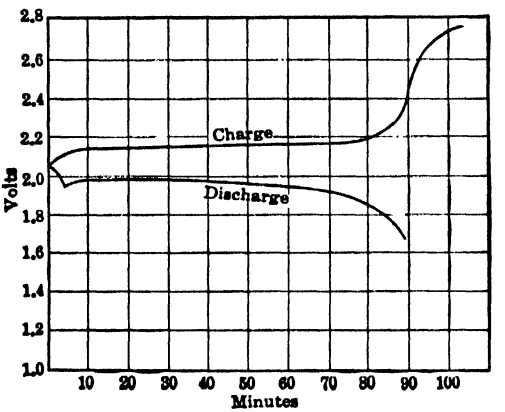

Fig. 160

portance, and is generally designated on the cell by the manufacturer. Cells should be charged until the voltage becomes constant and free evolution of gas has continued for at least two hours. During this period, no further increase in specific gravity of the electrolyte, as indicated by a hydrometer, should be noted. The value of the specific gravity of the electrolyte of a fully charged accumulator is 1.210 to 1.215. Fresh electrolyte should never be added to a cell until it has been determined that the proper specific gravity cannot be secured by charging alone. Sufficient distilled water should be added from time to time to insure the complete immersion of the electrodes in the solution. Care should be taken to remove any sediment which may collect in the battery jars before it comes in contact with the bottom of the electrodes.

The Nickel Oxide Accumulator. This secondary cell, invented by Edison and sometimes called the "Edison Battery," consists of two electrodes, one of nickelic oxide and the other of pure iron, immersed in a solution of potassium hydroxide, as indicated by the scheme,

$$Ni_2O_3 \mid KOH \mid Fe.$$

The reactions on charging and discharging the nickel oxide accumulator may be summarized by the equation

$$\mathrm{Fe} + 2\,\mathrm{Ni(OH)_3} \underset{\text{(charge)}}{\overset{\text{(discharge)}}{\rightleftarrows}} 2\,\mathrm{Ni(OH)_2} + \mathrm{Fe(OH)_2}.$$

The electrolyte is found to undergo no change during the operation of the cell. The initial normal electromotive force of the nickel oxide cell is 1.35 volts. Its ampere-hour efficiency is relatively low, amounting to approximately 82 per cent, while its watt-hour efficiency is only 59 per cent.

Depolarization and Electrolysis. As has previously been stated, an agent which is capable of lessening, or entirely eliminating, polarization is known as a depolarizer. Depolarizers can function in either of two ways. They may act as catalysts in accelerating the slow reaction which is responsible for the polarization, or they may act by reducing the energy consumption at the electrode to a value below that which corresponds to the equilibrium electrode potential. As an illustration of the first mode of action, the liberation of hydrogen at a cathode surface may be cited. While the polarization is often very great at the surface of ordinary metallic cathodes, it may be practically eliminated by the substitution of a platinized platinum electrode. The second mode of action of a depolarizer may be illustrated by the Bunsen primary cell, in which the anode is of zinc and the cathode of platinum or carbon, while both electrodes are surrounded by concentrated nitric acid. When weak acid only is used, the cathode reaction consists in the discharge of hydrogen ions, with a resultant electromotive force of about 0.7 volt. With concentrated acid, however, the cathode reaction is depolarized; hydrogen ions are no longer discharged but are oxidized to form water and the resultant electromotive force rises to approximately 1.0 volt. In other words, depolarization, in this case, consists in altering the former electrode process and substituting for it a reaction which takes place with the consumption of less energy. Depolarization may also be effected in some cases by purely mechanical means, such as vigorous stirring.

Both cathodic and anodic depolarizers are known. A cathodic depolarizer is a substance which readily undergoes reduction, whereas an anodic depolarizer is a substance which can be easily

oxidized. Numerous organic compounds are capable of functioning as depolarizers, due to the fact that many of them react with the products formed by the discharge of the ions. As a rule, the reactions involved in anodic depolarization are much more varied than those occurring in cathodic depolarization.

Electrolytic Reduction. When a depolarizer undergoes electrolytic reduction, the process may conveniently be considered as comprising two steps: (a) the initial step involving the formation of nascent, or active, hydrogen due to the discharge of hydrogen ions, as represented by the equation,

$$H^{\cdot} + \ominus \rightarrow H,$$

and (b), the reaction between the nascent hydrogen and the depolarizer. Since molecular hydrogen possesses relatively little reducing power, it is important to minimize its formation at the cathode during electrolytic reductions.

By varying the conditions under which a solution is electrolyzed, it is possible to obtain with the same depolarizer an entire series of different reduction products. For example, Haber* has shown that by the electrolytic reduction of nitrobenzene, $C_6H_5NO_2$, in both acid and alkaline solution under different experimental conditions, it is possible to obtain the following series of reduction products:

Nitrosobenzene	C_6H_5NO,
β-Phenylhydroxylamine	$C_6H_5 \cdot NH \cdot OH$,
Azoxybenzene	$C_6H_5 \cdot N(\rightarrow O) = N \cdot C_6H_5$,
Azobenzene	$C_6H_5 \cdot N = N \cdot C_6H_5$,
Hydrazobenzene	$C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$,
Aniline	$C_6H_5 \cdot NH_2$.

This illustrates in a striking manner the superiority of electrochemical reduction methods to ordinary chemical methods in which a different reducing agent is required for each reduction product, and where contamination by the reducing agent is almost certain to occur. In the foregoing series of reduction products of nitrobenzene, excellent yields of at least four of the substances — aniline, azoxybenzene, azobenzene and hydrazobenzene — can be

* Haber, Zeit. Elektrochem., **4**, 506 (1898); Zeit. phys. Chem., **32**, 193 (1900).

obtained by the electrolytic method by suitable control of temperature, cathode potential and the acidity or alkalinity of the solution.

Of the various factors affecting the efficiency of electrolytic reduction, the cathode potential is the most important. This quantity may be calculated by means of the equation,

$$E = -RT \ln \frac{k \cdot c_H}{c_{H^\cdot}}, \qquad (4)$$

where c_H is the concentration of the nascent hydrogen in the electrode, $c_{H^\cdot}$ the concentration of the hydrogen ions in the solution and k a constant. Since $c_{H^\cdot}$ may be assumed to remain practically constant, it follows that the cathode potential will vary directly with the concentration of the active hydrogen, and, therefore, according to the law of mass action, the reducing power of the cathode will be proportional to its potential.

Another important factor in electrolytic reduction is the velocity of depolarization. As has been pointed out, the electrolytic reduction of a depolarizer is a two-fold process which may be represented by the reactions,

(a) $H^\cdot + \ominus \rightarrow H$,

and (b) Depolarizer + H $\rightarrow$ Reduction product.

It is apparent that if the first reaction has a higher velocity than the second, the concentration of the active hydrogen will gradually increase and a corresponding increase in the cathode potential will occur. When the cathode potential reaches a certain value, gaseous hydrogen will be liberated at the electrode. The curves obtained by plotting cathode potentials against corresponding values of current strength afford an illustration of the foregoing statements. In Fig. 161, *ABCD* represents the curve of hydrogen evolution from an electrolyte containing no depolarizer, while *ABE* is the curve obtained with the same solution to which has been added a depolarizer which reacts rapidly with nascent hydrogen. It is important to note that the higher the velocity of depolarization, the more efficient is the reduction. Since the cathode potential increases with the current-density, it may happen, if too high current-densities are employed, that the potential-current curve will intersect the curve of hydrogen evolution, as in the

case of the curve *ABF* in Fig. 161. Since the point, *G*, at which these two curves intersect, corresponds to the cathode potential necessary for the liberation of gaseous hydrogen, it follows that a portion of the current will be consumed in producing gaseous hydrogen at the expense of a greater reduction of the depolarizer. Not only is the cathode potential increased by high current-density, but also the concentration of the depolarizer in the immediate vicinity of the cathode is lowered. It follows, therefore, that low current-densities tend to increase the efficiency of processes involving electrolytic reduction.

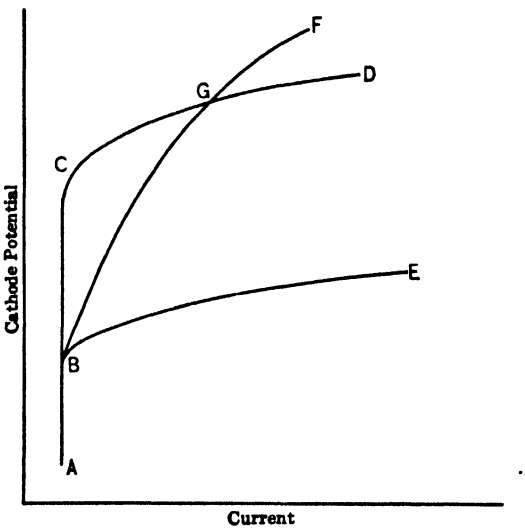

Fig. 161

There yet remains another factor which exercises a marked influence on the efficiency of electrolytic reduction processes. This third factor is the presence of catalysts in the electrolyte. It has been found that the presence of a small amount of an appropriate catalyst very appreciably accelerates the reaction between a depolarizer and the nascent hydrogen liberated at the cathode of an electrolytic cell. For example, the yield of hydroquinone obtained by the electrolytic reduction of an acid solution of quinone at a platinum cathode is greatly increased by the addition to the electrolyte of a minute quantity of titanic chloride. The latter is rapidly reduced at the cathode to the titanous salt,

and this in turn reduces the quinone to hydroquinone. The titanous salt, however, is oxidized in the process and the same cycle can thus be repeated indefinitely.

The cathode itself may also function as a catalyst. Cathodes of different metals have been found to accelerate the reaction between a given depolarizer and hydrogen at very different rates. As a consequence of this fact, the same reduction process can take place at a much lower cathode potential with some cathodes than with others. It follows, therefore, that at the same cathode potential, the permissible current-density can be widely varied. The influence of the nature of the cathode upon the current-

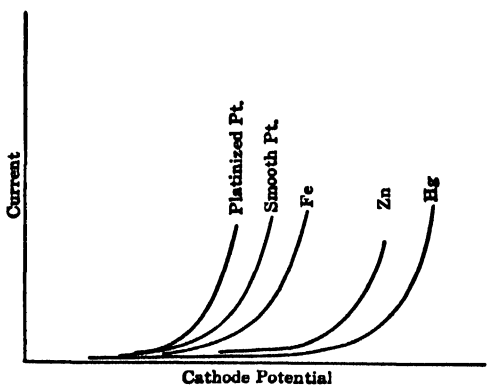

Fig. 162

potential curve is clearly shown in Fig. 162 where the results of a series of experiments with different electrodes employed in the reduction of an alkaline solution of potassium nitrate are represented graphically.

Electrolytic Oxidation. The principal anodic process involved in electrolytic oxidation processes is represented by the equation,

$$2\,OH' \rightarrow H_2O + \tfrac{1}{2}\,O_2 + 2\,\ominus.$$

This process is invariably accompanied by irreversible effects which render accurate measurements of the electrode potential impossible. In general it may be stated that the process of electrolytic oxidation closely resembles the process of electrolytic reduction, and the same generalizations which have been stated as applying to the one apply equally to the other. In electrolytic

oxidation processes, however, only a limited number of metals can be employed as anodes, since it is important that the electrodes should be attacked as little as possible by the products of electrolysis. The metals which fulfill this requirement most satisfactorily are platinum, iridium, palladium and iron, for processes occurring in alkaline solutions, while the platinum metals alone seem to be best adapted to electrolysis in acid solutions.

In carrying out electrolytic oxidations it is of the utmost importance that reduction of the products of oxidation at the cathode be prevented. This may be accomplished by the use of a porous diaphragm and a relatively small cathode surface which possesses a low hydrogen overvoltage. Cathodic reduction may also be prevented by adding to the electrolyte a small amount of potassium chromate. This causes the formation of a thin film of insoluble chromium chromate around the cathode and thus prevents the oxidation product from coming in direct contact with it.

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CHAPTER XIX

PHOTOCHEMISTRY

Radiant Energy. The visible portion of the spectrum is comprised between the extreme red, at one end, and the extreme violet at the other; the wave-length corresponding to the former is approximately 0.7 micron, while that corresponding to the latter is about 0.4 micron. The visible portion of the spectrum, however, is but a small fraction of the entire spectrum. Beyond the red of the visible spectrum lies the region of the so-called infra-red, comprising all wave-lengths from 0.76 micron up to 300 microns. Beyond the infra-red, between 300 and 2000 microns, is an unmeasured region, which is succeeded by the region of electrical waves, extending from 2000 microns to an undetermined maximum. On the other hand, extending beyond the violet of the visible spectrum is the so-called ultra-violet or actinic region, comprising all wave-lengths, between 0.4 micron and 0.1 micron. It thus appears that heat, light, and electricity are all forms of radiant energy, the only distinction between them being a difference in wave-length. Very little is known concerning radiant energy, and up to the present time all attempts to resolve it into a capacity and an intensity factor have failed. Whatever may be the nature of this form of energy, we know that the effects produced by it are dependent upon the wave-length of the radiation.

We have already devoted several chapters to the consideration of thermochemistry and electrochemistry, and it now remains to study, very briefly, the connection between chemical energy and that subdivision of radiant energy called light. This branch of theoretical chemistry is termed *photochemistry*.

The ultra-violet, or actinic rays are the most active chemically, although light of every wave-length, including the invisible infra-red, is capable of producing chemical action. When light falls upon a substance, a portion of the incident radiation is reflected, a portion is absorbed, and a portion is transmitted. It has been shown, that only that portion of the incident radiation which is absorbed is effective in producing chemical change.

Radiant energy has been shown by Lebedew,* and also by Nichols and Hull,† to exert a definite, though extremely small pressure. Thus, the pressure of solar radiations on the earth is equivalent to that of a column of mercury 1.4×10^{-9} mm. high.

Source of Radiant Energy. According to the electromagnetic theory of light, the emission of waves of light from a material source is due to the vibrations of minute charged particles called *radiators*. These radiators, which may be either atoms or electrons, give rise to electromagnetic waves of the same period as their own, that is, to light waves of definite length. The energy required to produce these electromagnetic waves is derived from the vibrating system itself, and unless an equivalent amount of energy is constantly supplied to the system, the amplitude of the vibrations will steadily diminish and ultimately cease.

There are two different ways in which this supply of energy can be maintained. First, the temperature of the vibrating system, as a whole, may be kept high. This type of radiation, which is maintained by purely physical means, is called *pure temperature radiation*. Every substance whose temperature is above the absolute zero (−273°) gives rise to pure temperature radiation. The higher the temperature, the more rapid and the more energetic the atomic and electronic vibrations become. With increase in rapidity of vibration, there results a corresponding diminution in wavelength, so that, as the temperature is raised, the longer heat waves are succeeded by the shorter waves of the visible region of the spectrum. When a sufficiently high temperature is reached, the period of vibration becomes so rapid as to cause the radiation of waves corresponding to the entire range of the visible spectrum. At higher temperatures, the rate of vibration is such that the vibrating particles must of necessity possess extremely small mass. It is commonly believed that under these conditions the vibration is wholly electronic.

The second way in which energy may be supplied to the vibrating atoms, or electrons, is by chemical or electrical means. The general term *luminescence* has been proposed by Wiedemann for all cases where luminous energy is derived from other sources than high temperature. It is to be observed, that luminescence is frequently exhibited by systems whose temperatures are compara-

* Rapp. pres au Congres de Physique, **2**, 133 (1900).

† Phys. Rev., **13**, 293 (1901).

tively low. For example, notwithstanding the fact that the flame resulting from the combustion of carbon disulphide has a temperature of only 150°, it has been found to be capable of affecting the photographic plate. Pure temperature radiation alone, at 150°, would correspond to long waves in the infra-red region of the spectrum and, as is well known, such waves are incapable of exerting appreciable photographic action.

Emission and Absorption. The relation between the emissive and absorptive powers of different bodies was first clearly enunciated by Kirchhoff * in 1859. This law may be stated as follows: — *Light of any given wave-length emitted by a body can also be absorbed by the same body at a lower temperature.* This law, it will be seen, offers a satisfactory explanation of the Fraunhofer lines in the solar spectrum. The sun is surrounded by a gaseous atmosphere, resulting from the vaporization of the elements present in the body of the sun. Each element in the cooler gaseous envelope, according to Kirchhoff's law, absorbs those wave-lengths which it emits at the higher temperature of the solar nucleus. The resulting dark lines of the solar spectrum have enabled the astronomer to determine the elementary composition of the sun.

If the emissive and absorptive powers of a body be denoted by E and A respectively, then according to Kirchhoff's law,

$$E/A = S, \tag{1}$$

where S is a constant. When absorption is complete, A is unity and $S = E$. Under these conditions the constant, S, may be defined as the emissivity of a body which absorbs all of the incident radiation and reflects none. Such a body was called by Kirchhoff a perfectly *black body.* The emissivity of a perfectly black body is equal to the ratio of the emissive to the absorptive power of any body at the same temperature. A familiar qualitative illustration of Kirchhoff's law is that afforded by the appearance of a fragment of white chinaware, decorated with a dark pattern, when heated to a high temperature. The dark parts of the design absorb light, while the white parts reflect it. On heating the fragment to redness, the pattern will be reversed, the dark portions of the design appearing bright, and the white portions dark.

It has been shown that the law of Kirchhoff is a necessary con-

* Ostwald's Klassiker, No. 100 (1898).

sequence of the application of the second law of thermodynamics to the thermal equilibrium within an enclosure whose walls are impervious to heat.

The Stefan-Boltzmann Law. From a study of the experiments of Dulong and Petit on the rate of cooling of different bodies, Stefan * discovered an empirical relation between the total radiation of a body and its temperature. Later, Boltzmann † derived the same relation thermodynamically and showed that instead of being general, as Stefan supposed, it is only strictly applicable to a perfectly black body. The Stefan-Boltzmann law may be stated as follows: — *The total radiation from a perfectly black body is directly proportional to the fourth power of the absolute temperature.* If the total radiation be denoted by S, we may write,

$$S = CT^4, \tag{2}$$

where C is a constant. If the radiation from the sun be considered solely as a temperature effect, its temperature may be calculated by the above equation expressing the Stefan-Boltzmann law. Employing available bolometric data, the temperature of the sun may thus be shown to be 6200° absolute.

The Displacement Law of Wien. Having considered the total energy radiated by a given source, we now come to the consideration of the distribution of energy throughout the entire spectrum in its relation to temperature. The results of the experiments of Lummer and Pringsheim ‡ on the distribution of energy in the normal spectrum of a black body are represented graphically in Fig. 163. The values of the energy radiated by the source are plotted as ordinates against the corresponding values of the wave-length as abscissæ. It will be observed that the energy corresponding to a definite wave-length increases with the temperature; and that each curve, or isothermal, exhibits a distinct maximum. The position of this maximum is displaced in the direction of decreasing wave-length as the temperature is raised.

In 1893, Wien § discovered the law governing this displacement of the energy maximum with temperature. If $\lambda_{max.}$ denotes the wave-length corresponding to the energy maximum, and T is the

* Sitz. Ber. Wiener Akad., 79 (II), 391 (1879).
† Wied. Ann., 22, 291 (1884).
‡ Verh. deutsch. phys. Ges., 1, 230 (1889); 3, 36 (1901).
§ Wied. Ann., 58, 662 (1896).

absolute temperature of the radiating black body, Wien showed that

$$\lambda_{max.} \times T = \text{constant.}$$

Furthermore, Wien found that

$$S_{max.} = BT^5, \qquad (3)$$

where $S_{max.}$ is the maximum emissivity corresponding to $\lambda_{max.}$ In general, the emissivity, S, is the amount of energy radiated per second from a narrow strip of the spectrum corresponding to the mean wave-length, λ. It should be mentioned, that while the experimental realization of a perfectly black body is impossible, a very close approximation can be obtained by the employment of a hollow blackened sphere, perforated by a small hole to permit the passage of the radiation. When this sphere is heated, practically all of the radiation is absorbed by multiple reflections at the inner surface. It has been found, that where such a black body is not available, or where extreme accuracy is not required, a thin strip of platinum foil coated with ferric oxide, and heated electrically, proves a satisfactory substitute. It is hardly necessary to call attention to the fact, that the term black body, as here used, does not imply a total absence of color. At high temperatures, a "black" source of radiation may be red, or even white. To avoid confusion, it has been proposed to substitute the term *full radiator* for the older term, black body.

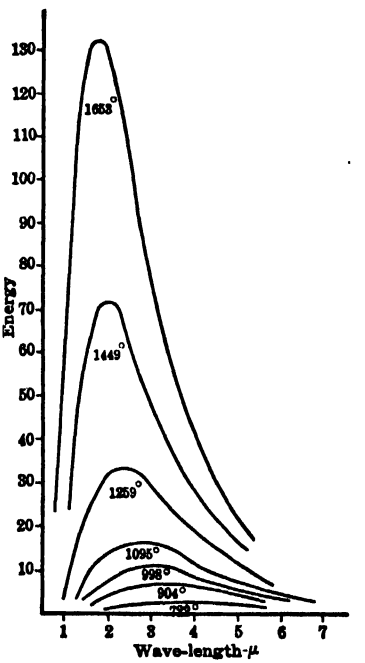


Fig. 163

Distribution of Energy throughout the Spectrum. The experimental determination of the radiant energy corresponding to a given wave-length, really resolves itself into the measurement of

the energy emitted between two contiguous wave-lengths, λ and $\lambda + d\lambda$. In other words, we actually measure the energy of a very small portion of the spectrum included between two wave-lengths which lie very close together.

Several different formulas have been proposed for the calculation of the distribution of energy throughout the spectrum. Of these, the formulas of Rayleigh and Wien have been found to reproduce experimental values with considerable accuracy. The formula of Rayleigh has the following form,

$$S_\lambda = \frac{CT}{\lambda^4} \cdot e^{-\frac{C'}{\lambda T}}; \tag{4}$$

while that of Wien may be written thus,

$$S_\lambda = \frac{C}{\lambda^5} \cdot e^{\frac{-C'}{\lambda T}}. \tag{5}$$

In these two formulas, C and C' are constants, while the other symbols have their usual significance. The formula of Rayleigh has been found to hold better in the region of the longer wave-lengths, while the reverse is true of the formula of Wien. It should be remembered, that both of these formulas apply only to bodies emitting continuous spectra.

The Quantum Theory. In attempting to give a complete theoretical interpretation of the curves shown in Fig. 163, Planck* was forced to the conclusion that radiation and absorption by an atom cannot proceed continuously. In other words, a vibrating atom is capable of absorbing or emitting energy only in integral multiples of a fundamental unit, or *quantum*, ϵ. This is known as the quantum hypothesis, or theory. Since, according to this theory, the energy of a vibrating atom can be absorbed, or emitted, only in amounts, ϵ, or in integral multiples of this magnitude, such as $2\,\epsilon$, $3\,\epsilon$, . . . $n\epsilon$, we are forced to conclude that energy, like matter, is not continuous but discrete.

This striking hypothesis differs so radically from the time-honored doctrine, that "Nature makes no leaps," that, despite the success attending Planck's effort to derive a formula which should conform to the experimental data on black-body radia-

* Planck, "Theorie der Wärmestrahlung."

tion, it is extremely doubtful whether the theory would have survived had it not been found to be equally applicable to such widely diverse phenomena as the variation of specific heats with temperature, the emission of electrons by metals when exposed to light, X-ray and optical spectra, ionization and resonance potentials and other seemingly unrelated phenomena. Although the quantum theory appears to be applicable in so many different directions, it is important to note that no one has as yet offered a satisfactory explanation as to why vibrating atoms should absorb and emit energy discontinuously. The quantum theory, therefore, is to be regarded as one of the unsolved puzzles of modern physics.

The magnitude of the quantum is not the same for all wave-lengths, but is directly proportional to the frequency, or inversely proportional to the wave-length. That is, for a frequency, ν, we may write

$$\epsilon = h\nu, \tag{6}$$

where h is a universal constant whose numerical value in absolute units is 6.55×10^{-27} erg-seconds. This important quantity is commonly known as "Planck's Constant." It is of interest to observe that the foregoing value of h represents the most probable value derived from determinations based on seven different methods in which the extreme variation of the results was not greater than 0.5 per cent.

The Photo-Electric Effect. In 1887, Hertz discovered that when a spark-gap is exposed to ultra-violet radiation, the voltage necessary for the passage of a spark is appreciably lowered. It was found that this effect was due to the emission of electrons, and the consequent ionization of the air between the terminals of the spark-gap.

The phenomenon was subsequently further investigated by Hallwachs* who found that when the surface of a clean piece of zinc was illuminated by ultra-violet light it lost the electric charge which it possessed. He also showed that an insulated piece of zinc acquired a positive charge when exposed to ultra-violet light, due to the emission of electrons. This phenomenon, which has since been found to be quite general, is known as the *photo-electric effect.*

* Hallwachs, Wied. Ann., 33, 301 (1888).

In the case of the alkali metals, a similar effect is produced by visible light, but for each surface there is found to exist a minimum frequency of radiation, ν_0, below which photo-electron emission ceases. As the frequency of the incident monochromatic radiation is increased above this limiting value, the velocity of the electrons emitted by the metal steadily increases. The number of electrons emitted is found to be directly proportional to the intensity of the incident radiation over a wide range of frequencies.

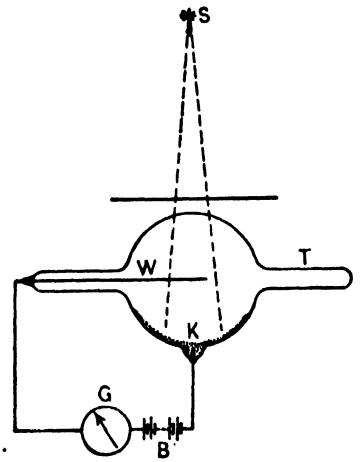


Fig. 164

This interesting effect has been utilized in the photo-electric cell which is probably the most sensitive instrument yet devised for the detection and measurement of radiation. A diagram of such a cell is shown in Fig. 164. A film of metallic potassium, K, is deposited *in vacuo* on the lower half of the inner surface of the tube, T. A platinum wire serves to connect this film with the negative terminal of a 300-volt battery, B, while the other terminal of the battery is connected through a sensitive galvanometer, or electrometer, G, with the platinum wire, W. When the upper half of the tube is exposed to incident radiation, the potassium emits electrons which are attracted to the positively charged wire, W, and thus a current is set up which produces a deflection in the galvanometer proportional to the intensity of the illumination. The sensitivity of a photo-electric cell unfortunately diminishes with time, whether it is in use or not.

According to Einstein,* the energy of photo-electrons varies directly with the frequency of the radiation, according to the equation,

$$\tfrac{1}{2} mv^2 = Ve = h\nu - h\nu_0, \qquad (7)$$

where m and v denote the mass and velocity of the electrons, respectively, V, the potential difference necessary to retard the velocity of the electron to zero, e, the electronic charge, ν, the

* Einstein, Ann. Physik, 17, 132 (1905); 20, 199 (1906).

frequency of the incident radiation, ν_0, the limiting frequency (sometimes termed the "photo-electric threshold") and h, Planck's constant. In equation (7), $h\nu$ measures the energy absorbed by the electron from the incident radiation, $h\nu_0$ represents the energy consumed in bringing the electron to the surface of the metal, while $\frac{1}{2}\ mv^2$ is the actual kinetic energy of the emergent electron. This latter magnitude is measured by the product Ve. A number of different metals have been examined by Millikan* with a view to testing the validity of equation (7) and, within the limits of experimental error, he has found that for any photo-electrically active surface, the maximum value of V increases linearly with the frequency, ν, of the incident radiation, the slope of the curve being given by the ratio of h to e. The mean value of h, as calculated from these experiments, is regarded as the most precise determination which has been made of this important constant.

Law of Photochemical Equivalence. With the introduction of the quantum theory into photochemistry it has been necessary to modify the views which have hitherto prevailed as to the relation between the energy of absorbed radiation and the resultant chemical change. Prior to the advent of the quantum theory numerous attempts had been made, particularly by Weigert, Trautz and Byk, to solve the problems of photochemistry by means of the methods of classical thermodynamics. These attempts, however, were only partially successful for reasons which are more or less obvious if the quantum theory is accepted. Indeed, it is claimed by Nernst and Noddack† that the only valid application of thermodynamics to photochemistry is in ascertaining whether, or not, a given dark reaction is possible under definite conditions.

In 1912, Einstein‡ proposed a theory of photochemical action in which he assumed that each molecule decomposed in a reaction requires the absorption of one quantum of radiation, $h\nu$, the frequency, ν, being characteristic of the absorbing molecule. This hypothesis has come to be known as the *law of photochemical equivalence*. Now if the energy absorbed per mol is U, it follows that

$$U = Nh\nu, \tag{8}$$

where N is Avogadro's constant.

* Millikan, Jour. Franklin Inst., 184, 337 (1917).

† Nernst and Noddack, Abstr. Jour. Chem. Soc., 123, ii, 526 (1923).

‡ Einstein, Ann. Physik (4), 37, 832 (1912).

The following table gives the values of $h\nu$ in ergs and U in calories for the wave-lengths corresponding to the entire visible and mid-ultra-violet spectrum.

ENERGY CORRESPONDING TO DIFFERENT PARTS OF SPECTRUM

Color.	Wave-length ($A°$).	$h\nu$ (ergs).	U (cal.).
Red	7500–6500	$2.62\text{–}3.02\times10^{-12}$	37800–43630
Orange	6500–5900	$3.02\text{–}3.33\times10^{-12}$	43630–48060
Yellow	5900–5750	$3.33\text{–}3.42\times10^{-12}$	48060–49320
Green	5750–4900	$3.42\text{–}4.01\times10^{-12}$	49320–57880
Blue	4900–4550	$4.01\text{–}4.32\times10^{-12}$	57880–62330
Violet	4550–3950	$4.32\text{–}4.97\times10^{-12}$	62330–71800
Ultra-violet	2000	9.9×10^{-12}	142000

Inspection of this table reveals the fact that very appreciable quantities of energy are involved when a chemical system absorbs light. Furthermore, it is apparent why photochemical reactions are more easily initiated by radiations of short wave-length.

A vast amount of experimental work has been carried out during the last decade with a view to testing the validity of the law of photochemical equivalence. The general character of these investigations may be indicated by a brief account of Bodenstein's* calculations, based upon Luther and Weigert's† studies of the polymerization of anthracene. When exposed to the light of the electric arc, anthracene undergoes polymerization according to the equation,

$$2\ C_{14}H_{10} \rightarrow (C_{14}H_{10})_2.$$

When 1 cc. of a solution of anthracene in anisole was exposed to the light from an arc lamp for 1 sec. at a distance of 1 cm. from the center of the arc — 1 sq. cm. of the solution being illuminated — it was found that the average amount of anthracene polymerized was 4×10^{-7} mols. On multiplying this by Avogadro's constant, we obtain $4\times10^{-7}\times6\times10^{23} = 2.4\times10^{17}$ molecules of anthracene polymerized per second. On computing, from the

* Bodenstein, Zeit. phys. Chem., **85**, 329 (1913).

† Luther and Weigert, Ibid., **51**, 297 (1905); **53**, 385 (1905).

estimated value of the energy of the absorbed radiation, the number of quanta involved, Bodenstein obtained 2×10^{17} quanta. In this case, therefore, the number of quanta absorbed is equal to the number of molecules reacting. It should be emphasized, however, that the law of photochemical equivalence does not apply equally well in all the cases which have been examined. This will be seen on inspecting the data of the following table in which the *quantum efficiency*, or the number of absorbing molecules which have reacted per quantum of absorbed radiation, is given for a number of photochemical reactions.

QUANTUM EFFICIENCY OF PHOTOCHEMICAL REACTIONS

Reaction.	Molecules/$h\nu$
$3\,O_2 \rightarrow 2\,O_3$	2
$2\,NH_3 \rightarrow N_2 + 3\,H_2$	0.25
$2\,O_3 + Cl_2 \rightarrow 3\,O_2 + Cl_2$	1
$H_2 + Cl_2 \rightarrow 2\,HCl$	2.8×10^6
$CH_3COCH_3 + H_2O \rightarrow CH_4 + CH_3COOH$	200
$CO + Cl_2 \rightarrow COCl_2$	100
$o\text{-}C_6H_4(NO_2)\cdot CHO \rightarrow o\text{-}C_6H_4(NO)\cdot CO_2H$	0.5

The actual values of the quantum efficiency will be observed to vary widely amongst themselves and to deviate greatly from the ideal value, namely unity. Because of these deviations, Plotnikow* and others have protested strongly against applying the term "law" to Einstein's relation. While it must be admitted that such results as those recorded in the foregoing table might easily lead one to suspect that the cases where the law does apply are merely fortuitous, Nernst and Noddack† have pointed out that while the first step in a photochemical reaction is undoubtedly the absorption of a single quantum by a single molecule, experimental verification of this fact is possible only for radiation confined within a restricted region of the spectrum, and when the reaction takes place under relatively simple conditions, since photochemical processes are, in general, accompanied by dark reactions which materially affect the amount of substance transformed.

* Plotnikow, Zeit. wiss. Photochem., **21**, 134 (1922).

† Nernst and Noddack, loc. cit.

High Temperature Thermometry.* Various optical methods for the measurement of high temperatures have been developed, but a detailed treatment of these methods is obviously out of place in a book of this character. Mention should be made, however, of two instruments which have proven of great value in high temperature measurements.

The optical pyrometer of Féry is based upon Stefan's law of total radiation. It consists of a telescope fitted with an objective of fluorite, at the focus of which is placed a sensitive thermocouple. In order to determine the temperature of a source of radiant energy, such as a crucible of molten metal, the telescope is directed toward the contents of the crucible and the image is focused on the thermo-junction by means of an adjustable eyepiece. The resulting electric current is then measured by means of a galvanometer.

In the optical pyrometer of Holborn and Kurlbaum, use is made of luminous radiations only. In this instrument, the current through a small incandescent lamp is varied until its light is just eclipsed by that from the hot body. When the point of balance has been reached, the incandescent filament and the hot body have the same temperature. The pyrometer is calibrated by determining the current necessary to raise the filament of the lamp to the temperature of the standard black body, the temperature of the latter being determined by means of a thermocouple. Of course, when the instrument is used to determine the temperature of sources of radiant energy which differ widely in character from that of a perfectly black body, the accuracy of the measurements is lessened, but even in an extreme case, such as that presented by polished platinum at 950°, the error does not exceed 74°. The importance of optical pyrometers in photochemical investigations lies chiefly in the determination of energy curves of light sources, and in the absolute measurement of radiant energy.

Luminescence. As has already been pointed out, it is customary to distinguish between pure temperature radiation and luminescence. The latter term is applied to all cases where chemical or electrical energy is transformed directly into radiant energy.

* For a detailed account of optical pyrometers, the student is referred to "High Temperature Measurements," by Le Chatelier and Boudouard, translated by Burgess (John Wiley and Sons, Inc.).

The various types of luminescence may be conveniently classified in the following manner:

Type of Luminescence	*Origin of Radiation*
(1) Photo-luminescence. (*a*) Fluorescence, (*b*) Phosphorescence.	Preliminary exposure of the luminous substance to some external source of radiant energy.
(2) Thermo-luminescence.	Stimulation by heat, but at a temperature considerably lower than that required for pure temperature radiation.
(3) Chemi-luminescence.	Chemical reaction.
(4) Tribo-luminescence.	Fracture or cleavage of crystals.
(5) Cathodo-luminescence.	Electric discharge.
(6) Radio-luminescence.	Radioactivity.

By the term *fluorescence* is meant the phenomenon of the emission, by an illuminated medium, of light of a different wave-length from that of the incident radiation. In general, the wave-length of the transformed radiation is greater than that of the incident radiation. This law, to which numerous exceptions have been discovered, was first enunciated by Stokes. When the incident radiation is cut off, fluorescence ceases.

Among the numerous substances which are known to exhibit the phenomenon of fluorescence, may be mentioned fluorite (from which the phenomenon derived its name), uranium glass, petroleum, solutions of organic dyestuffs, and quinine sulphate. The vapors of sodium, mercury, and iodine have been found by Wood to fluoresce brilliantly.

There are also many substances known which continue to emit light for some time after the external light-stimulus is removed. This phenomenon is termed *phosphorescence*, and appears to be governed by Stokes' law for fluorescence. The property of phosphorescence is apparently limited to anhydrous substances.

The sulphides of the alkaline earths may be mentioned as examples of phosphorescent substances. The investigations of Lenard and Urbain have revealed the interesting fact that the presence of a trace of one of the heavy metals greatly intensifies the light emitted by a phosphorescent substance.

The phenomenon of *thermo-luminescence* calls for little comment. There seems to be an intimate connection between thermo-luminescence and phosphorescence, since the substances exhibit-

ing the former phenomenon must be exposed initially to light, otherwise they do not emit any visible radiation on gentle heating.

Chemi-luminescence is a phenomenon which accompanies certain chemical reactions. Thus, Evans and Dufford* have shown that the oxidation of ethereal solutions of magnesium p-bromphenyl bromide gives rise to marked chemi-luminescence, the greenish-blue glow accompanying the reaction being visible in daylight.

When certain crystals, such as those of cane sugar, are either crushed, or simply rubbed together, flashes of light are emitted. This phenomenon is known as *tribo-luminescence.*

Cathodo- and *radio-luminescence* may be considered as subdivisions of the more inclusive term, *electro-luminescence.* Attention has already been called to the fact, that the residual gas in a vacuum tube is rendered luminous by the passage of the electric discharge, and also that certain minerals become phosphorescent when placed in the path of the cathode rays. These may be taken as examples of cathodo-luminescence. The luminosity of a screen coated with crystals of zinc sulphide, when subjected to the action of the α-particles shot out from a radio-active substance, will be mentioned in a subsequent chapter. This is clearly an instance of radio-luminescence.

Having briefly reviewed the different processes involved in the production of light we now turn to a consideration of the chemical phenomena resulting from exposure to light.

Photochemical Action. The development of the green color of plants under the influence of the rays of the sun, and the reverse process of bleaching in darkness, were probably the first photochemical reactions to be observed. To-day it is known, that light has the power of initiating, or accelerating, every variety of chemical change. This statement may be illustrated by the following typical photochemical reactions: — The polymerization of anthracene, the depolymerization of ozone, the transformation of maleïnoid into fumaroid forms, the hydrolysis of acetone, the oxidation of lead sulphide, and the reduction of silver salts. That such a variety of photochemical reactions should result from exposure to mixed, or heterogeneous, light is due to the selective absorption of each particular chemical system.

Photochemical action is not limited to the waves of the visible spectrum alone, but extends from the red end of the spectrum

* Evans and Dufford, Jour. Am. Chem. Soc. **45**, 278 (1923).

(wave-length 800 $m\mu$)* into the ultra-violet region (wave-length 200 $m\mu$). In fact, the shorter wave-lengths of the ultra-violet region of the spectrum have been found to be the most active photochemically.

Laws of Grotthuss. The two fundamental generalizations of photochemistry were first enunciated by Grotthuss, in 1818. These generalizations may be stated as follows:

(1) *Only those rays of light which are absorbed, produce chemical action.*

(2) *The action of a ray of light is analogous to that of a voltaic cell.*

It has been shown by Bancroft,† that the second of these two laws is inadequate to account for all of the known facts, and therefore, he proposes the following modification: — *All of the radiations which are absorbed by a substance tend to eliminate that substance. It is merely a question of chemistry whether any reaction occurs, and what the products of the reaction will be.*

Quantitative Relations Concerning the Absorption of Light. When a ray of light enters an absorbing medium, only a certain proportion of the incident radiation is absorbed. The intensity of the light entering an absorbing medium is not equal to that which is incident on the surface of the medium, owing to the fact that a portion of the incident beam is reflected. It has been found, that if the thickness of the medium be increased in arithmetical progression, the intensity of the transmitted light will decrease in geometrical progression. If the intensity of the light traversing a layer dl be denoted by I, then

$$-dI/dl = kI, \tag{9}$$

where k is a constant, depending upon the nature of the absorbing medium, and the wave-length of the light. This constant, k, is known as the *absorption index*. If the initial intensity of the light is I_0, and the total thickness of the medium is l, equation (9) becomes, on integrating,

$$I = I_0 \cdot e^{-kl}. \tag{10}$$

Or, equation (10) may be written in the form

$$k = \frac{1}{l} \ln \frac{I_0}{I}. \tag{11}$$

* 1 $m\mu = 10^{-7}$ cm.

† Jour. Phys. Chem., **12**, 209, 318, 417 (1908); **13**, 1, 181, 269, 449, 538 (1909); **14**, 292 (1910).

If we replace e^{-k} by α, then equation (10) becomes

$$I/I_0 = \alpha^l. \tag{12}$$

The constant, α, is called the *transparency*, or the *transmission coefficient.*

Bunsen and Roscoe introduced the term, *extinction coefficient.* This quantity may be defined, as the reciprocal of that thickness of the medium which reduces the intensity of the transmitted light to one-tenth of its initial value. If the extinction coefficient be denoted by ϵ, its value may be calculated from equation (10) in the following manner·

$$I = I_0 \cdot 10^{-\epsilon l}, \tag{13}$$

or

$$\epsilon = \frac{1}{l} \log \frac{I_0}{I}. \tag{14}$$

In 1852, Beer* enunciated an important law concerning the influence of concentration on absorption. Beer's law may be stated as follows: — *The absorption of light by different concentrations of the same solute dissolved in the same solvent is an exponential function of the concentration, provided the thickness of the absorbing medium be maintained constant.* It follows from this law, that

$$I = I_0 \alpha^{cl}, \tag{15}$$

where c is the concentration of the solution.

If Beer's law is valid, the ratio, $c/\epsilon = A$, known as the *absorption ratio,* should be constant. Beer's law has been tested with a large number of solutions and has been found to hold only in those cases where no change in the solute occurs when the concentration of the solution is altered.

Photochemical Extinction. According to the first law of Grotthuss, only the absorbed light is chemically active. The converse of this law, viz., that every substance which absorbs light undergoes chemical change, apparently does not hold. Furthermore, only a portion of the rays absorbed by a light-sensitive substance are directly involved in effecting chemical change. For example, while an alkaline copper tartrate solution shows marked absorption in the infra-red, red, yellow, and ultra-violet, it has been proven, that the photochemical reduction of the copper salt to cuprous oxide is due to the action of the ultra-violet rays alone.

The first quantitative measurements of the absorption of light

* Pogg. Ann., 86, 78 (1852).

by a reacting system were made by Bunsen and Roscoe.* These investigators found that the absorption of light by hydrogen and chlorine, taken separately, was less than the absorption of the reacting mixture of the two gases. From this result, they concluded that in a photochemical reaction, the absorption of light by the reacting system is greater than the sum of the individual absorptions of the reacting substances. The absorption of light by the reacting system, over and above the ordinary, or "optical" absorption of the reacting substances, they called *photochemical extinction*. While the phenomenon of photochemical extinction is regarded by many physical chemists as having doubtful significance, nevertheless the distinction between purely optical absorption on the one hand, and chemical absorption on the other, is quite generally accepted.

If the distinction drawn by Bunsen and Roscoe between optical and chemical absorption be accepted, then all photochemical reactions may be regarded as belonging to one, or the other, of two classes, as follows: — (1) reactions in which light does work against chemical affinity, the work being equivalent to the photochemical extinction; or (2) reactions in which the light functions merely as a catalyst. In reactions belonging to the first class, the light is considered to be the agent which actually initiates chemical change, whereas in reactions of the second class, the light is assumed to accelerate reactions which would otherwise proceed at a slower rate.

Kinetics of Photochemical Reactions. Let A and B represent two chemically distinct substances, and let us assume that the reaction,

$$A \rightarrow B,$$

takes place under the influence of light. The course of the reaction can be followed in the usual manner, by determining the amount of either constituent which is present at any definite time. There are certain factors, however, which render such kinetic measurements more difficult in the case of a photochemical reaction than in that of an ordinary chemical reaction. Let us assume that the above reaction is homogeneous and of the first order, and also that it takes place in homogeneous solution. It is apparent that if the system is illuminated from one side, as shown

* Ostwald's Klassiker, No. 38.

in Fig. 165, the rate at which A undergoes transformation into B will depend upon the thickness, d, of the absorbing layer. Hence, if the velocity of the transformation be denoted by dB/dt, we may write,

$$dB/dt = k[A], \tag{16}$$

in which the value of the constant, k, will not only be a function of the intensity and wave-length of the light, but also of position. Furthermore, the variation in the velocity of the reaction in successive layers will cause differences in concentration which will tend to become equalized by the process of diffusion. From this example, it is obvious that the extent to which light is absorbed is dependent upon the dimensions of the absorbing system.

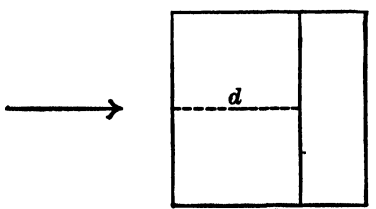


Fig. 165

If light be regarded as a material substance, then we may conveniently consider its absorption as analogous to the diffusion of a gas into a liquid, and the light intensity at any point may be regarded as the analogue of concentration, or active mass. According to the law of mass action, the velocity of a chemical reaction is expressed by the equation,

$$dx/dt = kc_1^{n_1} \cdot c_2^{n_2} \cdot \cdots - k'c_1'^{n_1'} \cdot c_2^{n_2'} \cdot \cdots,$$

where c_1, c_2, etc., are the concentrations of the substances entering into the reaction, and n_1, n_2, etc., are the coefficients derived from the chemical equation, and indicating the order of the reaction. In applying this equation to photochemical reactions, the following possibilities must be borne in mind:

(1) The reaction may take place in successive stages. Under these conditions the experimentally measured velocity will correspond to that of the slowest reaction.

(2) Side reactions may occur, with the formation of products quite different from those resulting from the main reaction.

(3) There may be catalysis. In fact, this phenomenon is frequently met with in the study of photochemical reactions. Nernst has pointed out that the velocity constants, k and k', in the foregoing equation, may conveniently be considered as being directly proportional to the intensity of the light, for light

of the same wave length. Owing to the absorption of the medium, this intensity will be a function of position in the medium. In applying the law of mass action to photochemical reactions, it is important to note that, as a general rule, the exponents n_1, n_2, etc., in the equation of the so-called *dark-reaction*, are not identical with the exponents ν_1, ν_2, etc., of the *light-reaction*. In other words, the order of a chemical reaction is usually different in the light from what it is in the dark. The photochemical exponents ν_1, ν_2, etc., are never greater than, and are seldom equal to, the corresponding exponents n_1, n_2, etc., of the dark-reaction.

Thus, Bodenstein * showed that the dissociation of hydriodic acid, in the dark, is a reaction of the second order and may be represented by the equation,

$$2\,HI \rightleftarrows H_2 + I_2,$$

whereas, when hydriodic acid dissociates in the light, the reaction is of the first order, as shown by the equation,

$$HI \rightleftarrows H + I.$$

In this case, the light merely accelerates the velocity of the dark-reaction.

The action of light on the reverse reaction may be such as to oppose its usual course in the dark. In this case, the resulting photochemical equilibrium, or so-called *photo-stationary state*, will not be identical with the corresponding chemical equilibrium. It should be observed, that the photo-stationary state differs from ordinary chemical equilibrium, in that its permanency is wholly dependent upon the constancy of the source of illumination; i.e., when the light is cut off, the photo-stationary state shifts to the ordinary chemical equilibrium, provided the reaction is reversible. It has also been found that the temperature coefficients of most photochemical reactions are negligible.

Becquerel † discovered that silver chloride, which had been precipitated in the dark, was only sensitive to short wave-lengths of light, whereas silver chloride, which had been exposed for a few moments to sunlight, became sensitive to all wave-lengths in the visible spectrum, and also to the shorter wave-lengths of the infra-red. This phenomenon, which has been observed with various sub-

* Zeit. phys. Chem., **22**, 23 (1897).

† Ann. Chim. Phys. [3], **9**, 257 (1843).

stances, was first studied systematically by Bunsen and Roscoe,* who termed it *photochemical induction.* Employing a mixture of hydrogen and chlorine gases, they found that under constant illumination, the velocity of formation of hydrochloric acid, which was hardly appreciable at first, increased rapidly to a maximum, and then remained constant. The interval of time required for the reaction to attain its maximum velocity is known as the *period of induction.* It has been found, that in almost every photochemical reaction there is a similar period of initial perturbation. The phenomenon has been thoroughly investigated by Burgess and Chapman,† who arrived at the conclusion, that induction effects are to be ascribed to the presence of minute traces of various impurities, such as gases or water vapor, adsorbed by the walls of the reaction-vessel. We may therefore conclude that induction effects are not characteristic of photochemical reactions.

Classification of Photochemical Reactions. According to Sheppard, ("Photochemistry,") photochemical reactions may be conveniently classified in the following manner:

(1) Reversible reactions, i.e., reactions in which the products formed under the influence of light react to reproduce the original system when the light is removed.

(2) Irreversible reactions, i.e., reactions in which the light promotes transformation to a more stable system. Irreversible reactions are subdivided into —

(a) Complete reactions; and

(b) Pseudo-reversible reactions.

The polymerization of anthracene may be taken as an example of a reversible photochemical reaction. This reaction may be represented as taking place according to the equation,

$$2\,C_{14}H_{10} \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} C_{28}H_{20},$$

the upper arrow indicating the direction of the light-reaction (polymerization), and the lower arrow that of the dark-reaction (de-polymerization).

An illustration of a completely irreversible photochemical reaction is afforded by a mixture of hydrogen and chlorine gases

* Pogg. Ann., 100, 481 (1857).

† Jour. Chem. Soc., 89, 1402 (1906).

which combine, on exposure to light, to form hydrochloric acid gas, according to the equation,

$$H_2 + Cl_2 \xrightarrow{\text{light}} 2\,HCl.$$

If the hydrochloric acid is removed by solution in water as fast as it is formed, the velocity of the reaction will be directly proportional to the intensity of the light. Bunsen and Roscoe * made use of the foregoing facts in the construction of their actinometer.

The reduction of ferric oxalate may be taken as an example of a pseudo-reversible photochemical reaction. This substance is reduced to ferrous oxalate on exposure to light as shown by the equation,

$$Fe_2(C_2O_4)_3 \xrightarrow{\text{light}} 2\,Fe\,(C_2O_4) + CO_2.$$

In the dark, ferrous oxalate is re-oxidized to ferric oxalate by the oxygen of the air. While the initial substance is reproduced, it is evident that the reaction is not strictly reversible.

Actinometers. A number of different forms of apparatus have been devised for measuring the chemical action of light; such instruments are known as *actinometers.*

The hydrogen-chlorine actinometer is based upon the well-known fact, that the speed of the reaction between hydrogen and chlorine varies greatly with the intensity of illumination. Bunsen and Roscoe,† guided by the experiments of Draper, constructed an actinometer in which the rate of combination of hydrogen and chlorine could be measured, by allowing the hydrochloric acid formed to dissolve in water, and noting the resulting diminution of volume. A diagram of this apparatus is given in Fig. **166.**

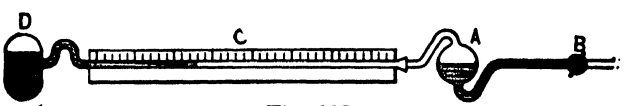


Fig. **166**

The apparatus is filled with a mixture of equal parts of hydrogen and chlorine, obtained by the electrolysis of a solution of hydrochloric acid. The bulb *A*, containing water, is connected at one end with a tube fitted with a stop-cock *B*, and at the other end

* "Photochemische Untersuchungen," Ostwald's Klassiker, No. 34.

† Pogg. Ann., 100, 43 (1857); 101, 235 (1857).

with a horizontal tube terminating in a reservoir D, which also contains water. When the water has become saturated with the constituents of the gaseous mixture, B is closed and the entire apparatus is protected from light. When it is desired to measure the photochemical action of a source of light, the bulb A is uncovered and the light is allowed to fall upon it. Some of the hydrogen and chlorine will combine, and the hydrochloric acid formed will be absorbed by the water in A; the column of water in the horizontal tube will move to the right, the magnitude of the movement being measured on the scale C. In this manner, the amount of photochemical action can be determined. An objection to the use of hydrogen and chlorine in the actinometer is the danger of violent explosions when the illumination is too intense. To remove this objection, Burnett replaced the hydrogen of the mixture by carbon monoxide.

The Ultraviolet Radiometer. Quite recently, Anderson and Robinson* have developed a very convenient actinometer for the quantitative measurement of ultraviolet radiation which they designate as an *ultraviolet radiometer*. These authors have shown that the photochemical decomposition of oxalic acid, in the presence of uranyl sulphate as a sensitizer, is admirably adapted to the accurate and rapid measurement of ultraviolet radiation. In setting up the radiometer two standard solutions are required, which are prepared according to the following directions: (1) Exactly 6.3 grams of pure oxalic acid crystals and 4.27 grams of uranyl sulphate ($UO_2SO_4 \cdot 3\,H_2O$) are dissolved in distilled water and diluted to 1 liter. This solution must be kept in the dark. (2) An approximately 0.1 N solution of potassium permanganate is standardized against the oxalic acid solution.

In order to make a relative determination of the amount of ultraviolet radiation from a given source, it is only necessary to expose to the light exactly 25 cc. of solution (1) in a transparent fused-quartz vessel. After a period of time, depending upon the intensity of the radiation, the sample is removed and titrated against solution (2). The result may then be stated in milligrams of oxalic acid decomposed, or may be calculated to ergs.

In making a relative determination it is, of course, necessary to maintain exactly similar conditions and each time to irradiate the

* Anderson and Robinson, Jour. Am. Chem. Soc., 47, 718 (1925).

same volume and area of solution. This method is adaptable to the measurement of the energy radiated by any source of ultraviolet light.

Absolute measurements of light are usually recorded in ergs per second per sq. cm. It is, therefore, necessary to note the area of surface of the solution exposed to the radiation. For this purpose a rectangular quartz cell is very convenient; this should be so constructed that a thickness of solution ranging from 1.5 to 2 cm. can be secured. The cell should be so arranged that the incident radiation may enter the solution through one side only. In measuring the distance between the light source and the cell, the center of the solution, and not the wall of the cell, is to be taken as the point of measurement. In an atmosphere which is practically dust-free the law of inverse squares may be applied with accuracy for distances less than 40 cm. Under the conditions outlined, 1 mg. of oxalic acid decomposed in 30 minutes, corresponds to the following number of ergs absorbed at the corresponding wave-lengths:

Wave-length	*Ergs per Second*
2550 Å	4.18×10^5
3020	5.04
3650	5.27
Complete ultraviolet	4.84

The length of exposure of the solution to the illumination depends entirely upon the intensity of the radiation. Frequently five or ten minutes will suffice, and then again an hour or more may be required.

In this connection it should be emphasized that in all accurate photochemical measurements, both the intensity and the wave-length of the source of radiation must be specified.

Action of Light on the Silver Halides. Probably the most familiar, and undoubtedly one of the most important, photochemical reactions is that which takes place on the exposure of a photographic plate.* Luther† has shown that when a pure sil-

* For an excellent treatment of the chemistry of photography the student is recommended to consult " Photography for Students of Physics and Chemistry," by Louis Derr (Macmillan); or " Photochemie und Beschreibung der photographischen Chemikalien," by H. W. Vogel.

† Zeit. phys. Chem., 30, 628 (1899).

ver halide is exposed to light, it undergoes reduction according to the equation,

$$2\ AgX \xrightarrow{light} Ag_2X + X,$$

where X may be chlorine, bromine, or iodine. On removing the light, the sub-halide recombines with the free halogen as shown by the equation,

$$Ag_2X + X \xrightarrow{dark} 2\ AgX.$$

In other words, the reaction is strictly reversible and a well-defined photo-stationary state results from a given intensity of illumination. The investigations of Baker* make it appear quite probable, that the photochemical reduction of the silver halides is dependent upon the presence of a minute trace of water vapor as a catalyst. In the photographic plate, the silver halide is embedded in gelatine, which not only accelerates the rate of reduction of the silver halide, but also causes the reaction to become irreversible. The alteration in the behavior of the silver halide, brought about by the presence of gelatine, is due to the fact that the latter reacts with the free halogen, according to the equation,

$$2\ AgBr + \text{gelatine} \xrightarrow{light} Ag_2Br + \text{brominated gelatine}.$$

The continuous removal of the liberated bromine by the gelatine is an example of what is known as *photochemical sensitization*. Another example of photochemical sensitization is afforded by a mixture of benzene and silver chloride. The normal darkening of the silver salt is markedly increased by the presence of the benzene, which combines with the chlorine as rapidly as it is set free by the action of the light on the silver halide.

While the silver bromide of the photographic plate is extremely sensitive to the shorter wave-lengths, corresponding to the violet and ultra-violet regions of the spectrum, it is only reduced by the longer wave-lengths after prolonged exposure. It has been found, however, that the addition of certain dyestuffs, such as eosine and Congo-red, renders the silver halide sensitive to the longer wave-lengths of the spectrum. This phenomenon, which is known as *optical sensitization*, must be carefully distinguished from chemical

* Jour. Chem. Soc., 61, 782 (1892.)

sensitization, to which reference has already been made. It is to be noted that an optical sensitizer does not absorb, chemically, any of the products of the reaction. Photographic plates which have been sensitized in this way are commonly known as orthochromatic plates.

All of the dyestuffs which can function as optical sensitizers have been found to exhibit anomalous refraction; i.e., for wave-lengths slightly longer than those absorbed, these substances possess an abnormally large refractive index, in consequence of which the refracted waves exert the same effect upon the silver halide as the shorter wave-lengths of the spectrum. Although it is not an essential property, it is generally found that optical sensitizers are fluorescent. As an example of optical sensitization, where the sensitizer is non-fluorescent, we may take the photochemical reduction of mercuric chloride in the presence of ammonium oxalate. This reaction takes place according to the equation,

$$2\,HgCl_2 + (NH_4)_2C_2O_4 \xrightarrow{\text{light}} Hg_2Cl_2 + NH_4Cl + 2\,CO_2.$$

The presence of the non-fluorescent ferric ion, $Fe^{\cdots}$, has been shown by Winther* to be an effective optical sensitizer in the foregoing reaction. The ferric ion is reduced to the ferrous state, while the oxalic acid undergoes oxidation. It was pointed out by Eder† that this reaction is well adapted for actinometric measurements, since the amount of mercurous chloride precipitated is directly proportional to the intensity of the light.

Photochemical After-Effect. Certain photochemical reactions are known in which the reaction has been found to proceed even after the light stimulus is removed. This phenomenon is known as the *photochemical after-effect*. The velocity of a reaction of this kind is different from that of either the light-, or the dark-reaction. It has also been found, that if a portion of the reaction-mixture, which has already been exposed to the light, be added to a fresh unexposed portion, the latter immediately commences to decompose. Thus, a solution of iodoform in chloroform becomes brown, on exposure to light, due to liberation of iodine. If the solution is removed from the light, the decomposi-

* Zeit. wiss. Phot., 7, 409 (1909).

† Sitz. ber. Wien. Akad. (1879).

tion will continue for several days, while if a small portion of the partially decomposed solution be added to a freshly prepared solution, the latter will commence to decompose. The photochemical after-effect can be readily explained, if we assume that the action of light gives rise to heterogeneous nuclei, which persist for a sufficient time after the light is removed to act as centers around which the reaction can proceed throughout the unexposed portion of the mixture.

Assimilation of Carbon Dioxide. A photochemical reaction of special interest to the biologist is that in which atmospheric carbon dioxide is taken up by plants, under the influence of solar radiation. While the reaction is exceedingly complex, it may be regarded as taking place according to the hypothetical equation,

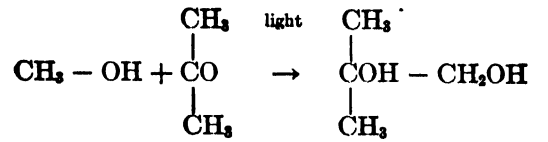
$$6\ CO_2 + 5\ H_2O \xrightarrow{\text{light}} \underset{\text{(starch)}}{C_6H_{10}O_5} + 6\ O_2.$$

This reaction represents a gain in energy amounting to approximately 685 calories per formula-weight of starch. It is quite probable, however, that the initial product of the reaction is formaldehyde, and that subsequently the latter substance undergoes polymerization, with the formation of starch and other carbohydrates. The green coloring matter of the leaves of plants, known as chlorophyll, also plays an important part in the assimilation of carbon dioxide, but beyond the fact that its action is not catalytic, little can be stated as to the manner in which it functions in the reaction. The velocity of the reaction has been found to attain its maximum value in yellow and green light, a result which is in complete agreement with the fundamental law of Grotthuss, that only those rays which are absorbed are active chemically. As has already been stated, the temperature coefficients of photochemical reactions are generally very small. This is not true, however, of the reaction under consideration. It has been found that the rate at which carbon dioxide is assimilated by a plant is nearly doubled for a rise in temperature of 10° (see p. 438).

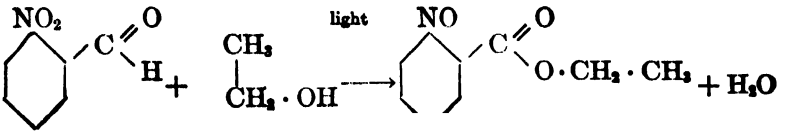
Photochemical Synthesis. While it has long been known that light is capable of effecting in the living plant the synthesis of complex organic compounds from carbon dioxide and water, it is only recently that its efficiency in bringing about a great variety of organic reactions has been fully recognized. Owing to the re-

searches of Ciamician and others in this field, numerous photochemical syntheses of considerable practical value to the organic chemist have been discovered. It must suffice here to mention a few such typical photochemical syntheses.

Alcohols may be oxidized in successive steps, the action of the light closely resembling the action of ferments. Methyl alcohol and acetone react to form isobutylene glycol according to the equation,



The action of light has been found to be especially favorable to such processes as the foregoing, involving reciprocal oxidation and reduction. Ortho-nitro-benzaldehyde, in the presence of ethyl alcohol, reacts to form the ethyl ester of o-nitroso-benzoic acid, as shown by the equation,



One of the most interesting and suggestive developments in the realm of photochemistry is the synthesis of formaldehyde and carbohydrates by Baly and Heilbron.* These investigators showed that when an aqueous solution of carbon dioxide is agitated and exposed to ultraviolet radiation of wave-length 200 $m\mu$, appreciable amounts of formaldehyde are formed. Furthermore, an aqueous solution of formaldehyde was found to undergo polymerization to reducing sugars under the influence of ultraviolet radiation of wave-length 290 $m\mu$. The photosynthesis of formaldehyde from aqueous solutions of carbon dioxide was shown to be readily photocatalyzed by various colored basic substances, such as the colloidal hydroxides of iron and uranium. In the presence of these catalysts, the photosynthesis can be effected by the wave-lengths of the visible spectrum. When a concentrated aqueous solution of potassium bicarbonate was irradiated by a mercury lamp, considerable quantities of formaldehyde were produced,

* Baly and Heilbron, Jour. Chem. Soc., 119, 1025 (1921).

but in insufficient amounts to give a positive test for reducing sugars. If, however, some pure formaldehyde was added to the solution, a positive test for reducing sugars was obtained within a few hours.

Thus, for the first time, we have experimental confirmation of the much disputed hypothesis of Baeyer that the formation of formaldehyde is the initial step in the photosynthesis of the complex compounds found in living plants.

Further interesting results have since been obtained by Baly, Heilbron and Hudson,* who have extended their studies in photosynthesis to the formation of nitrogen compounds. It has long been known from the work of the botanist, Schimper, that nitrites are invariably present in the leaves of living plants in the dark, but that these compounds disappear on exposure to light, provided chlorophyll is present. It had also been observed by Baudisch † that formhydroxamic acid is produced when aqueous solutions of potassium nitrite containing methyl alcohol are exposed to light. With these two experimental observations as a starting point, Baly and his co-workers commenced their investigations on the photosynthesis of nitrogen compounds. They showed that activated formaldehyde — such as is produced by the action of ultraviolet light of wave-length 200 $m\mu$ on an aqueous solution of formaldehyde — readily combines with potassium nitrite to give formhydroxamic acid. This latter compound can immediately react with other molecules of activated formaldehyde to produce a large variety of complex substances, such as those found in the living plant. These investigators have concluded that the formation of formhydroxamic acid marks the first stage in the photosynthesis of all of the nitrogen compounds found in plants. The reaction may be represented by the following equations:

$$\underset{\text{Activated formaldehyde}}{H-C-OH}+O=N-OK \rightarrow \begin{matrix} H-C-OH \\ \| \\ O=N-OK \end{matrix} \rightarrow \underset{\text{Formhydroxamic acid (Potassium salt)}}{\begin{matrix} H-C-OH \\ \| \\ N-OK \end{matrix}} +O.$$

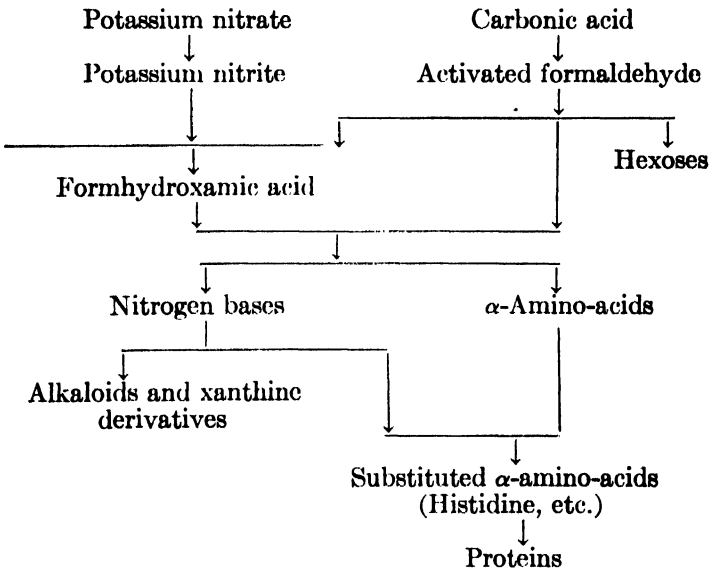
They have obtained definite evidence of the formation of α-amino-acids, one of which, a substituted α-amino-acid, they believe to be

* Baly, Heilbron and Hudson, Ibid., 121, 1078 (1922).

† Baudisch, Berichte, 44, 1009 (1911).

histidine, while a crystalline alkaloidal base closely resembling and possibly identical with glyoxaline has been isolated.

The following scheme has been advanced as an indication of the possible lines along which the photosynthesis of the complex compounds occurring in plants may proceed:



It is significant that many of the results obtained by Baly and his colleagues working with ultraviolet light have recently been confirmed by Dhar and Sanyal * in tropical sunlight.

The far-reaching importance of investigations of the character of those just outlined is emphasized by Baly in the following words:

" The interaction of the activated formaldehyde with formhydroxamic acid follows two main lines, the formation of amino-acids and of various nitrogen bases. These nitrogen bases consist of various types, namely pyrrole, pyridine, and glyoxaline, which by further condensation with activated formaldehyde give indole, quinoline, isoquinoline, and xanthine derivatives. In cases where such is possible, these bases condense with amino-acids to give the substituted amino-acids such as histidine, tryptophan, etc. The excess of nitrogen bases undergoes further condensation to give alkaloids, whilst the substituted amino-acids interact to give proteins. The readiness with which all of these reactions take place is due to the cardinal fact that the various compounds are produced in highly reactive phases, analogous to the highly reactive phase of

* Dhar and Sanyal, Jour. Phys. Chem., 29, 926 (1925).

formaldehyde, when photosynthetically formed. This reactivity enables condensations to occur which are otherwise impossible to realize in the laboratory. It is a matter of common knowledge that these reactions must occur in the living plant, and our results show that the key to the problem is the enhanced reactivity of freshly synthesized molecules. The synthesis of the nitrogen compounds found in the plant is not photosynthetic, except in so far as the production of the activated formaldehyde by the chlorophyll is concerned. The various amino-acids, proteins, alkaloids, etc., are the natural, and indeed inevitable, results of the photosynthesis of formaldehyde in the presence of potassium nitrite."

In attempting to repeat the experiments of Baly and his coworkers, Spoehr * failed to secure a positive test for the presence of formaldehyde and, therefore, concludes that Baly either omitted certain essential details in the account of his work, or else that he misinterpreted his experimental observations.

Baly's experiments on the photosynthesis of formaldehyde from carbon dioxide in the presence of a dye-stuff, such as malachite green, have also been repeated by Baur and Büchi † with the result that they attribute the formation of the formaldehyde to the reduction of the dye and not to the reduction of the carbon dioxide.

It is apparent, therefore, that further research is necessary before it can be stated with certainty that the photosynthesis of formaldehyde and sugar from carbon dioxide and water has been effected.

Photoelectric Cells. The absorption of light by any one of the three states of matter is invariably accompanied by a change in electrical condition. The different electric effects accompanying the absorption of radiant energy have been classified by Sheppard in the following manner:

(1) Ionization with a corresponding increase of conductance in gases, liquids, and solids, caused by transmission of light.

(2) Indirect ionization of a gas, due to reflection, or emission of electrons from the surface of a contiguous denser phase.

(3) Development of electromotive forces in cells of the following type:

Electrode A (light)	Conductor, Di-electric	Electrode A, (dark)

where the two electrodes are separated by a medium which is partially a conductor and partially a di-electric.

* Spoehr, Jour. Am. Chem. Soc., **45**, 1185 (1923).

† Baur and Büchi, Helv. Chim. Acta, **6**, 959 (1923).

The treatment of the first and second of these three classes of photoelectric phenomena properly lies within the domain of pure physics. The third class, however, includes a number of photogalvanic combinations of considerable interest and importance to the physical chemist.

The first investigation of photoelectric combinations was undertaken by E. Becquerel,* in 1839. He prepared a cell consisting of identical plates of pure silver, coated with a silver halide, and immersed in dilute sulphuric acid as an electrolyte. On exposing one electrode to the light, while the other was kept in the dark, an appreciable electromotive force was developed, the current flowing in the solution from the darkened to the illuminated electrode. If a galvanometer be included in the circuit, the deflection of the needle may be taken as a measure of the intensity of the light.

The action of the Becquerel actinometer has been explained by Ostwald as follows: — The incident light lessens the stability of the silver iodide, which undergoes ionization according to the equation,

$$AgI \rightarrow Ag^{\cdot} + I',$$

the $Ag^{\cdot}$ ions giving up their charges to the electrode, while the I' ions enter the solution. For every $Ag^{\cdot}$ ion which is discharged at the illuminated electrode, an equal number of $Ag^{\cdot}$ ions enter the solution at the darkened electrode, thus charging the latter negatively. Hence the current flows, in the solution, from the darkened to the illuminated electrode.

Rigollot† constructed an electrical actinometer in which the silver plates used by Becquerel are replaced by two oxidized copper electrodes, while a dilute solution of sodium chloride is used instead of dilute sulphuric acid.

A number of photoelectric combinations have been investigated by Wildermann,‡ among which he recommends the following as being especially suitable for actinometers:

(a) $\underset{\text{(light)}}{Ag} \mid AgBr, 0.1\ N\ KBr \mid AgBr \mid \underset{\text{(dark)}}{Ag},$

Reaction, $2\ AgBr \rightarrow Ag_2Br$

(b) $\underset{\text{(light)}}{Cu} \mid CuO \mid NaOH \mid CuO \mid \underset{\text{(dark)}}{Cu},$

Reaction, $2\ CuO \rightarrow Cu_2O.$

* Ann. Chim. Phys. [3], 9, 257 (1843).

† Jour. de Phys. [3], 6, 520 (1897).

‡ Plotnikow's "Photochemische Versuchstechnik" is recommended as an excellent guide to practical laboratory methods.

Of these two cells, the latter is perhaps the better, since it gives an appreciable electromotive force for light of the same intensity and varying wave-length.

While all of the theoretical interpretations of the action of photoelectric cells are more or less inadequate, the investigations of Scholl and others make it appear probable that negative electrons enter the electrolyte from the electrode, while positive ions are discharged on the electrode, thereby causing anodic polarization. In general the direction of the photoelectric current inside the cell is from the non-exposed to the exposed electrode.

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CHAPTER XX

THE ELECTRICAL THEORY OF MATTER

Conduction of Electricity through Gases. Within recent years the discovery of new facts relative to the conduction of electricity through gases has led to the development of the so-called *electron* or *corpuscular theory of matter*. Under ordinary conditions, gases are practically non-conductors of electricity, but when a sufficiently great difference of potential is established between two points within a gas, it is no longer able to withstand the stress, and an electric discharge takes place between the points. The potential necessary to produce such a discharge is quite high, several thousand volts being required to produce a spark of one centimeter length in air at ordinary pressures. The pressure of the gas has a marked effect upon the character of the discharge and the potential required to produce it. If we make use of a glass vessel similar to that shown in Fig. 167, the effect of pressure on the nature of the discharge may be studied. This apparatus consists of a straight glass tube about 4 cm. in diameter and 40 cm. long, into the ends of which platinum electrodes are sealed. To the side of the vessel, a small tube is sealed so that connection may be established with an air-pump and manometer. If the electrodes are connected with the terminals of an induction coil, and the pressure within the tube be gradually diminished, the following changes in the character of the discharge will be observed. At first, the spark becomes more uniform and then broadens out, assuming a bluish color. When a pressure of about 0.5 mm. is reached, the negative electrode, or *cathode* will appear to be surrounded by a thin luminous layer; next to this will be found a dark region, known as the *Crookes' dark space;* adjoining this will be found a luminous portion, called the *negative glow,* and beyond this will be seen another dark region, which is

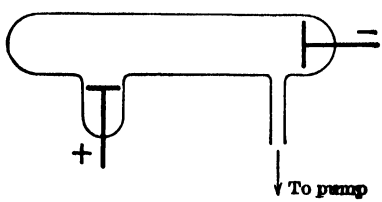

Fig. 167

frequently referred to as the *Faraday dark space.* Between the Faraday dark space and the positive electrode, or *anode* is a luminous portion, called the *positive column.* By a slight variation of the current and pressure, the positive column can be caused to break up into alternate light and dark spaces or *striæ*, the appearance of which is dependent upon various factors, such as the nature of the gas and the size of the tube. If the pressure in the tube be diminished to about 0.01 mm., a new phenomenon will be observed. The positive column will vanish, and the walls of the tube opposite the cathode will become faintly phosphorescent. The color of the phosphorescence will depend upon the nature of the glass. If the tube is made of soda glass, the glow will be greenish yellow, while with lead glass the phosphorescence will be bluish. The phosphorescence is due to the bombardment of the walls of the tube by very minute particles projected normally from the cathode. These streams of particles are called the *cathode rays.*

Some Properties of Cathode Rays. The following are among the most important properties of the cathode rays:

1. *The cathode rays travel in straight lines normal to the cathode, and cast shadows of opaque objects placed in their path.* This property may be demonstrated by means of a vacuum tube in which a small metallic Maltese cross is interposed in the path of the rays. When the current passes, a distinct shadow of the cross is cast on the opposite wall of the tube. The cross may be hinged at the bottom so that it can be dropped out of the path of the rays, when the usual phosphorescence will be obtained.

2. *The cathode rays can produce mechanical motion.* By means of an apparatus devised by Sir William Crookes, this property of the cathode rays may be demonstrated. Within a vacuum tube is placed a small paddle wheel which rolls horizontally on a pair of glass rails. When the current is applied to the tube, the wheel will revolve, moving away from the cathode. By reversing the current, the wheel will stop, and then rotate in the opposite direction, owing to the reversal of the direction of the cathode stream.

3. *The cathode rays cause a rise of temperature in objects upon which they fall.* If a small piece of platinum is placed at the center of curvature of a spherical cathode in a vacuum tube, and a strong discharge be sent through the tube, the anode will begin to glow,

and if the action of the current be continued long enough, the platinum plate may be rendered incandescent, thus showing the marked heating effect of the cathode rays.

4. *Many substances become phosphorescent on exposure to the cathode rays.* If the cathode rays be directed upon different substances, such as calc-spar, barium platino-cyanide, willemite, scheelite and various kinds of glass, beautiful phosphorescent effects may be observed. This phosphorescent property is useful in observing and experimenting with the cathode rays.

5. *The cathode rays can be deflected from their rectilinear path by a magnetic field.* If a phosphorescent screen is placed opposite to the cathode in a vacuum tube, a circular phosphorescent spot will appear when the tube is excited. If the tube be placed between the poles of an electromagnet, the phosphorescent spot will move at right angles to the direction of the magnetic field. On reversing the polarity of the magnet, the spot will move in the opposite direction. Furthermore, the direction of the deflection will be found to be similar to that produced by a negative charge of electricity moving in the same direction as the cathode ray.

6. *The cathode rays can be deflected from their rectilinear path by an electrostatic field.* If two insulated metal plates, are sealed into the sides of a vacuum tube, parallel and opposite to each other, and a difference of potential of several hundred volts be applied to the plates, the luminous spot produced by the rays on a phosphorescent screen will be found to move, the direction of the motion being the same as that of a negatively charged body under the influence of an electrostatic field. Reversal of the field, causes the phosphorescent spot to move to the opposite side of the screen.

7. *The cathode rays carry a negative charge.* Probably the most important characteristic of the cathode rays is their ability to carry a negative charge. While the magnetic and electrostatic deviation of the rays made this fact more than probable, it remained for Perrin to demonstrate, that a negative electrification accompanies the cathode stream A modification of Perrin's apparatus, due to Sir J. J. Thomson, is shown in Fig. 168. It consists of a spherical bulb to which is sealed a smaller bulb, and a long side tube. The small bulb contains the cathode, C, and the anode, A. The anode consists of a tight-fitting brass plug pierced by a central hole of small diameter. The side tube, which is out of the direct range of the cathode rays, contains two coaxial metallic

cylinders, insulated from each other, each being perforated with a narrow transverse slit. One of these, *D*, is earth-connected, while *B* is connected with an electrometer, by means of the rod, *F*. When the tube has been pumped down to the proper pressure for the production of cathode rays, a phosphorescent spot will appear at *E*,

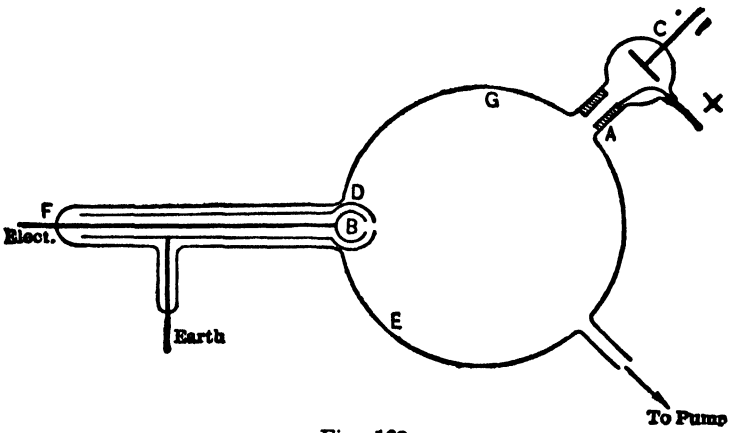

Fig. 168

directly opposite the cathode, *C*. Upon testing *B* for possible electrification by means of the electrometer, it will be found to be uncharged. If the cathode stream be deflected by means of a magnet, so that the rays fall upon *B*, a sudden charging of the electrometer will be observed, proving that *B* is becoming electrified. Upon deflecting the rays still further, so that they are no longer incident upon *B*, the accumulation of the charge will immediately cease. If the electrometer be tested for polarity, it will be found to be negatively charged, thus proving the charge carried by the cathode rays to be negative.

8. *The cathode rays can penetrate thin sheets of metal.* In 1894, Lenard constructed a vacuum tube fitted with an aluminium window opposite the cathode. He showed, that the cathode rays passed through the aluminium, and are absorbed by different substances outside of the tube, the absorption varying directly with the density of the substance

9. *The cathode rays when directed into moist air cause the formation of fog.* This phenomenon has been shown by C. T. R. Wilson to be due to the minute particles in the cathode stream acting as nuclei upon which the water vapor can condense.

Velocity of the Cathode Particle. Since the cathode rays consist of minute, negatively-charged particles which can be deflected by a magnetic and an electrostatic field, it is possible to measure their speed, and to compute the ratio of the mass of a particle to its charge. The special form of tube shown in Fig. 169 was devised for the purpose by Sir J. J. Thomson. It consists of a glass tube about 60 cm. in length, furnished with a flat cir-

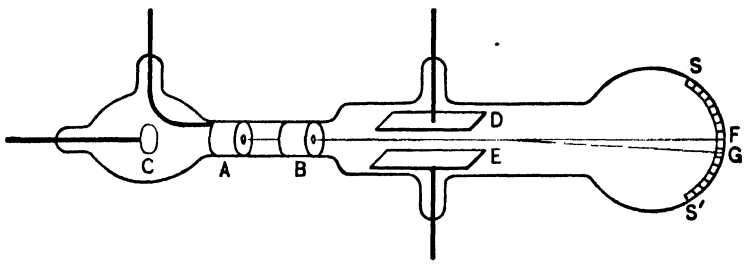

Fig. 169

cular cathode, C, and an anode, A, in the form of a cylindrical brass plug about 2.5 cm. in length, pierced by a central hole 1 mm. in diameter. Another brass plug, B, is placed about 5 cm. away from A, the two holes being in exactly the same straight line, so that a very narrow bundle of rays may pass along the axis of the tube and fall upon the phosphorescent screen at the opposite end of the tube. Upon this screen is a millimeter scale, SS'. Two parallel plates, D and E, are sealed into the tube for the purpose of establishing an electrostatic field. When the tube is connected with an induction coil, or other source of high-potential, a phosphorescent spot will appear at F. If a strong magnetic field be applied, the lines of force being at right angles to the plane of the diagram, the rays will be deflected vertically, and the spot on the screen will move from F to G. Let H denote the strength of the magnetic field, and let m, e and v represent, respectively, the mass, charge and velocity of a cathode particle. A magnetic field, H, acting at right angles to the line of flight of the cathode particle will exert a force, Hev, which will tend to deflect the particle from a rectilinear path. This force must be equal to the centrifugal force of the moving particle acting outwards along its radius of curvature. Therefore,

$$Hev = \frac{mv^2}{r},$$

or
$$Hr = \frac{mv}{e}. \tag{1}$$

Since H and r can both be measured, the ratio, $\frac{mv}{e}$, can be determined. Now if a difference of potential be established between D and E, and the lines of force in the electrostatic field have the proper direction, it will be possible to alter the strength of the field so as just to counterbalance the effect of the magnetic field, and bring the phosphorescent spot back to F again. Under these conditions, if X denotes the strength of the electrostatic field, we have

$$Xe = Hev,$$

or
$$v = \frac{X}{H}. \tag{2}$$

Since X and H can both be measured, v can be calculated, and, by introducing the value so obtained into equation (1), the ratio e/m can be evaluated. By this method, the average value of v has been found to be 2.8×10^9 cm. per second, while 5.30×10^{-17} electrostatic units is the mean value of the most trustworthy determinations of the ratio, e/m.

Charge Carried by the Cathode Particle. Until the value of the charge carried by the cathode particle has been determined, it is clearly impossible to compute its mass. Only a brief outline of the method employed to determine this quantity can be given here. Upon suddenly expanding a volume of saturated water vapor, its temperature is lowered with the simultaneous formation of a cloud, each particle of dust present serving as a nucleus for a fog particle. If sufficient time be allowed for the mist to settle and the vapor to become saturated again, a repetition of the preceding process will result in the formation of less mist, owing to the presence of fewer dust particles. By repeating the operation enough times, the space may be rendered dust free. As has already been pointed out, cathode particles serve as nuclei for the condensation of water vapor, their function being similar to that of dust particles. It has been shown by Sir George G. Stokes, that if a drop of water of radius r, be allowed to fall through a gas of viscosity η, then the velocity with which the drop falls will be given by the equation,

$$v = \frac{2}{9} \cdot \frac{gr^2}{\eta}, \tag{3}$$

where g is the acceleration due to gravity. The viscosity of air at any temperature being known, a cloud can be produced by expansion of water vapor in the presence of cathode particles in an appropriate chamber. The speed, v, with which the cloud falls can be measured, and hence r can be calculated by means of equation (3). If m is the total mass of the cloud, and n is the number of drops per cubic centimeter, then

$$m = 4/3\ n\pi r^3 \text{ (density of water } = 1).$$

A simple application of thermodynamics enables one to calculate the value of m. Knowing the values of m and r, the number of drops in the cloud, n, which is the same as the number of cathode particles, can be calculated. It is a simple matter to measure the total charge in the expansion chamber, and if this be divided by the total number of charged particles, the charge carried by a single particle will be obtained. The latest determinations show this to be 4.774×10^{-10} electrostatic units. This being practically identical with the calculated value of the charge on the hydrogen ion in electrolysis, it follows, that the mass of the cathode particle is 1845 times less than the mass of the atom of hydrogen, or 0.00054 on the scale of atomic weights in which O = 16. The cathode particle has the smallest mass yet known and has been called the *corpuscle* or *electron*.

An ingenious modification of the foregoing method, based upon the fact that when X-rays are passed through air or any other gas some of the molecules are broken up into positively or negatively charged carriers of electricity called ions, has enabled Millikan * to determine the value of e with extreme accuracy. A sketch of the apparatus used by him is shown in the accompanying illustration, Fig. 170. A finely divided spray of oil, or some other liquid is introduced into the chamber, D, by means of the atomizer, A, until one of the tiny drops eventually finds its way through the aperture, p, into the space between the two condenser plates, M and N. The hole, p, is then closed and the air between the plates is ionized by means of the X-ray tube, X. The arc lamp, a, serves to illuminate the drop, and its motion is observed through a microscope, not shown in the figure. The eye-piece of the microscope is fitted with an engraved glass scale, which enables the observer to measure accurately the motion of the drop. When

* Phys. Rev. 39, 349 (1911); 2, 143 (1913).

the drop collides with one of the ions of the air in the condenser chamber, it acquires an electric charge, the sign of which will determine the subsequent direction of its motion with reference to M and N. By means of the switch, S, the signs of the charges on the two plates can be reversed, thus causing a corre-

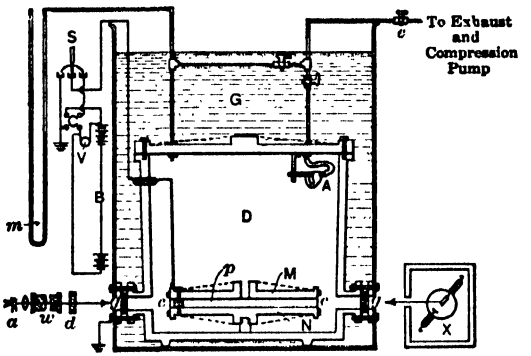

Fig. 170

sponding reversal of the direction of motion of the drop. By careful adjustment of the difference of potential between the plates, it is possible to keep the drop in the field of view during an entire experiment. Any change in the speed of the drop is an indication of a change in the charge which it carries. Therefore, since the speed with which the drop moves is directly proportional to the magnitude of its charge, it follows, that by measuring the change of speed and comparing it with the speed of the drop when falling under the influence of gravitational attraction alone, the value of the charge carried by the drop can be calculated.

In this manner Millikan found that the total charge on the drop was invariably an exact integral multiple of the elemental electronic charge, e. It was observed that seven or eight electronic charges were quite commonly acquired by a single drop, but in every case the total charge was invariably an exact integral multiple of the elemental charge, e. The value of e given by Millikan as the mean of a large number of determinations is 4.774×10^{-10} electrostatic units: this result is believed to be in error by less than 0.1 percent. In the following table are given some of the more recently determined values of e, as found by several observers using different experimental methods.

VALUES OF THE ELEMENTAL ELECTRIC CHARGE, e

Observer	Method	e in e.s.u.
Millikan	Oil or mercury	4.77×10^{-10}
Begeman	Water drops	4.67×10^{-10}
Roux	Sulphur drops	4.17×10^{-10}
Ehrehaft	Metallic dust	4.65×10^{-10}
Rutherford	Counting α-particles	4.65×10^{-10}
Planck	Radiation data	4.69×10^{-10}

Avogadro's Constant. The ratio of mass to charge for the hydrogen ion in electrolysis is known to be 1.04×10^{-4} and, as we have seen, the value of the charge is identical with that carried by the electron viz., 4.774×10^{-10} electrostatic units, or 1.57×10^{-20} electromagnetic units. It follows, therefore, that the mass, m, of the hydrogen atom must be $1.04 \times 10^{-4} \times 1.57 \times 10^{-20} = 1.63 \times 10^{-24}$ grams. Having established the weight of the hydrogen atom in grams, the weight in grams of the atom of any other element can be calculated from the ratio of its atomic weight to the atomic weight of hydrogen. The mass of one cubic centimeter of hydrogen, measured under standard conditions of temperature and pressure, is 8.81×10^{-5} grams; hence the number of atoms present in one cubic centimeter of hydrogen, under standard conditions, is $8.81 \times 10^{-5} \div 1.63 \times 10^{-24} = 5.41 \times 10^{19}$. Since the molecule of hydrogen is diatomic, it follows that the number of molecules contained in one cubic centimeter must be $5.41 \times 10^{19} \div 2 = 2.705 \times 10^{19}$. But one gram-molecule of any gas, when measured under standard conditions, occupies 22400 cc.; therefore, the number of molecules present in one gram-molecule is, $22400 \times 2.705 \times 10^{19} = 6.06 \times 10^{23}$. This fundamental quantity is known as *Avogadro's Constant.* A table of the values of this constant, as determined by different observers using different methods, is given on p. 24.

Positive Rays. As we have seen, the cathode rays consist of negatively charged particles which are repelled from the cathode of a vacuum tube. These particles, or electrons, under the influence of a high potential, move with an enormous velocity, and, by collision with the atoms of the residual gas within the tube, they remove one or more electrons from these atoms, leaving them with a positive charge. These positively-charged atoms are

immediately repelled by the anode, and move with high velocity toward the cathode. If a tube with a perforated cathode be used, these positively charged atoms will pass through the perforations into the space behind the cathode, where their properties may be studied. These rays have been called *positive rays* by Sir J. J. Thomson, who has developed an ingenious method for the determination of the individual masses of the positively charged particles constituting the rays. While this method of analysis of positive rays has proved of great value for a general survey of masses and velocities, it leaves much to be desired as a method of precision.

The defects in Thomson's method have been overcome, in large measure, by Aston,* who has recently perfected an apparatus for positive-ray analysis which he calls a "mass spectrograph." This instrument is illustrated diagrammatically in Fig. 171. The

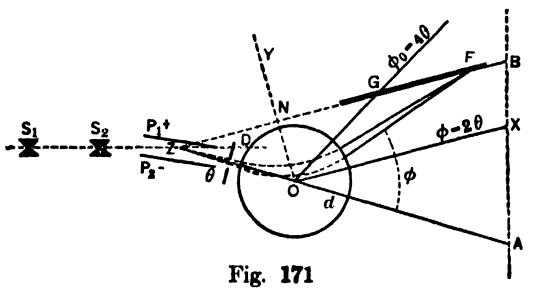

Fig. 171

positive rays after reaching the cathode, pass through two narrow parallel slits of special construction, S_1S_2, which permit a thin ribbon of rays to pass between the charged plates, P_1 and P_2, where they are spread out into an electric spectrum under the influence of the electric field. After emerging from the electric field, the rays may be considered as radiating from a virtual source Z, midway through the field on the line, S_1S_2. A portion of the emergent rays, deflected through an angle, θ, from their initial direction is sorted out by means of a diaphragm, D, and allowed to pass between the parallel poles of a powerful electro-magnet, O. The strength of the magnetic field is such, that the rays are deflected backward through an angle, ϕ, which is more than twice as great as θ. By this means, all of the rays having a given ratio of charge to mass, are brought to a focus, F, where an image is

* Phil. Mag., 38, 709 (1919).

produced on a photographic plate, *GF*. In this way, each class of charged particles will produce its own image at its own particular focus. The resulting series of images is known as a *mass spectrum*. By measuring the displacement of the image produced by a particle of unknown mass, and comparing this with the corresponding displacement of the image produced by a particle whose mass is known, it is possible to determine the mass of the unknown particle. Since in a mass spectrum, all measurements are relative, any known element may be selected as a standard. Obviously, oxygen is taken as the standard, its molecule, its singly-charged atom, and its doubly-charged atom giving reference lines at 32, 16 and 8, respectively. In a mass spectrum, the displacement with increasing mass is very nearly linear, hence, if the distances from a chosen point of reference are d_1 and d_2, and if m_1 and m_2 are the corresponding masses, it follows, that for given values of d_1 and d_2, the value of the ratio, m_1/m_2, will be the same in every experiment. It is estimated that atomic weights can be determined in this manner with an accuracy of 0.1 per cent. Small amounts of carbon monoxide and carbon dioxide are frequently mixed with the gas under investigation in order to promote the smooth running of the discharge tube, while traces of hydrocarbons, derived from stop-cock lubricants, are almost invariably present.

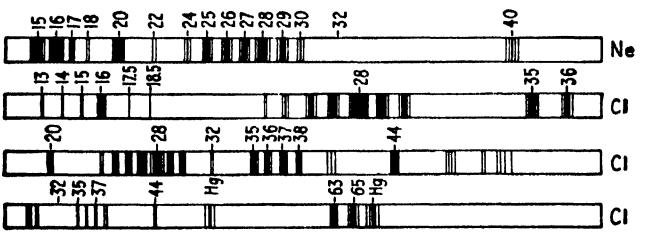

Fig. 172

A reproduction of the mass spectra of neon and chlorine is given in Fig. 172. The relative masses, taking oxygen as a standard, are indicated by the accompanying numbers. The prominent lines in the neon spectrum correspond to 0 = 16, C_2 = 24, C_2H_2 = 26 and C_2H_4 or CO = 28, while the two lines produced by neon itself are found to correspond to atomic weights 20.0 and 22.0, rather than to 20.2, the commonly accepted atomic weight of neon. From this result, Aston concludes that neon

is made up of two species of atoms differing in atomic weight by two units. A mixture of nine parts by weight of the lighter atoms with one part by weight of the heavier atoms, would give a gas whose atomic weight would correspond to that assigned to neon in the table of atomic weights.

In like manner, the mass spectrum of chlorine shows intense lines at 16, 28 and 44; these are undoubtedly due to the presence of oxygen, carbon monoxide and carbon dioxide respectively, while the strong lines at 35.0, 36.0, 37.0, and 38.0 are believed to indicate the existence of two different species of chlorine atoms, one of which has an atomic weight of 35.0 and the other an atomic weight of 37.0. The other two lines at 36.0 and 38.0 are attributed to the presence of the corresponding hydrogen compounds, HCl′ and HCl″, where Cl′ = 35.0 and Cl″ = 36.0.

As will be pointed out in the following chapter, the somewhat revolutionary idea that substances can exist with practically identical chemical and spectroscopic properties and yet differ in atomic weight, was advanced by Soddy and others, several years before Aston furnished direct experimental evidence of the fact. In attempting to find a place for the radio-elements in the periodic table, Soddy found it necessary to assign certain elements to the same position in the table, and hence proposed that such elements should be called *isotopes*.

Recent investigations by Aston* on the methods of production of positive rays have resulted in the development of a new procedure, which he terms the method of "accelerated anode rays," whereby the difficulties hitherto encountered in the production of the mass spectra of a number of the metallic elements are eliminated. In this new method, which has proven to be of quite general application, Aston employs the anode rays from a composite cathode of graphite and metallic salts. In this manner he has succeeded in demonstrating that the lighter elements also exist as isotopes and that the masses of isotopic elements are whole numbers within the limits of experimental error, which in most cases does not exceed one part in a thousand.

The accompanying table gives the results of Aston's determinations of the mass-numbers of isotopes of the elements thus far investigated.

* Aston, Phil. Mag., 47, 385 (1924).

MASS-NUMBERS OF ISOTOPES

Element	Atomic No.	Atomic Wt.	Minimum No. of Isotopes.	Mass-numbers of Isotopes in Order of Intensity.
H	1	1 008	1	1
He	2	4 00	1	4
Li	3	6 94	2	7, 6
Be	4	9 02	1	9
B	5	10 82	2	11, 10
C	6	12.00	1	12
N	7	14 01	1	14
O	8	16 00	1	16
F	9	19 00	1	19
Ne	10	20 20	2	20, 22
Na	11	23 00	1	23
Mg	12	24 32	3	24, 25, 26
Al	13	26 96	1	27
Si	14	28 06	3	28, 29, 30
P	15	31.02	1	31
S	16	32 06	1	32
Cl	17	35 46	2	35, 37
A	18	39.88	2	40, 36
K	19	39 10	2	39, 41
Ca	20	40 07	2	40, 44
Sc	21	45 10	1	45
Ti	22	48 10	1	48
V	23	51 00	1	51
Cr	24	52 00	1	52
Mn	25	54 93	1	55
Fe	26	55.84	2	56, 54
Co	27	58 97	1	59
Ni	28	58 68	2	58, 60
Cu	29	63 57	2	63, 65
Zn	30	65 38	4	64, 66, 68, 70
Ga	31	69 72	2	69, 71
Ge	32	72.38	3	74, 72, 70
As	33	74 96	1	75
Se	34	79 20	6	80, 78, 76, 82, 77, 74
Br	35	79 92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80, 78
Rb	37	85 44	2	85, 87
Sr	38	87 63	2	88, 86
Y	39	88 90	1	89
Zr	40	(91)	(4)	90, 94, 92, (96)
Ag	47	107 88	2	107, 109
Cd	48	112 41	6	114, 112, 110, 113, 111, 116
In	49	114 80	1	115
Sn	50	118 70	7 (8)	120, 118, 116, 124, 119, 117, 122, (121)
Sb	51	121.77	2	121, 123
Te	52	127.5	3	128, 130, 126
I	53	126 92	1	127
X	54	130.20	7 (9)	129, 132, 131, 134, 136, 128, 130, (126), (124)
Cs	55	132.81	1	133
Ba	56	137.37	(2)	138, (136)
La	57	138 91	1	139
Ce	58	140 25	2	140, 142
Pr	59	140 92	1	141
Nd	60	144 27	(4)	142, 144, 146, (145)
Hg	80	200 60	(6)	(197), 202, 204, 198, 199, 200
Bi	83	209.00	1	209

(Numbers in parentheses are provisional only.)

Aston's investigations have thus established the unitary theory of matter and thereby have confirmed, after more than a century of discussion, the essential correctness of the hypothesis of Prout.

The discovery of isotopes also furnishes a satisfactory explanation of the inversion of the positions of argon and potassium, of

tellurium and iodine, and of cobalt and nickel in the periodic table. Thus, according to Aston's table, argon, with an atomic weight of 39.88, has two isotopes whose weights are 40 and 36, respectively, the former being present in greater amount. In like manner, potassium has two isotopes whose weights are 39 and 41, respectively, the former predominating. The investigations of Moseley — outlined in a succeeding chapter — have shown that the nuclear charge of the isotopes of argon is one less than the nuclear charge of the isotopes of potassium. The inversion in the position of the two elements is, therefore, to be ascribed to the difference in the relative amounts of the two isotopes which are present in each.

In addition to the positive-ray method, already outlined, several other methods have been developed for the separation of isotopes. Of these, we may mention the methods based upon diffusion,* fractional distillation,† and free evaporation,‡ each of which has been found to yield interesting results.

Thus, Harkins and Madorsky§ employing a large steel apparatus by means of which 2.5 kg. of mercury could be dealt with in a single experiment, and making use of a special cooling device which enabled them to draw off fractions continuously, succeeded in obtaining a light fraction of mercury at the end of a period of 268 hours which showed a decrease in atomic weight of 0.044 of a unit, and, simultaneously, a heavy fraction which showed an increase in atomic weight of 0.052 of a unit.

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* Harkins, Jour. Am. Chem. Soc., **42**, 1328 (1920); **44**, 37 (1922).

† Lindemann, Phil. Mag. **37**, 523 (1919); **38**, 173 (1919).

‡ Brönsted and Hevesy, Phil. Mag., **43**, 31 (1922); Zeit. phys. Chem., **90**, 189 (1921).

§ Harkins and Madorsky, Jour. Am. Chem. Soc. **45**, 591 (1923).

CHAPTER XXI

RADIOACTIVITY

Discovery of Radioactivity. The first radioactive substance was discovered by Henri Becquerel,* in 1896. It had been shown by Roentgen in the previous year, that the bombardment of the walls of a vacuum tube by the cathode stream, gives rise to a new type of rays, which, because of their puzzling characteristics, he called X-rays. The portion of the tube where these rays originate was observed to fluoresce brilliantly, and it was at once assumed that this fluorescence might be the cause of the new type of radiation.

Many substances were known to fluoresce under the stimulus of the sun's rays, and it was natural, in the light of Roentgen's discovery, that all substances which exhibit fluorescence should be subjected to careful examination. Among those who became interested in these phenomena was Becquerel. He studied the action of a number of fluorescent substances, among which was the double sulphate of potassium and uranium. This salt, after exposure to sunlight, was found to emit a radiation capable of affecting a carefully protected photographic plate. Further investigation proved that the fluorescence had nothing to do with the photographic action, since both uranous and uranic salts were found to exert similar photographic action, notwithstanding the fact that uranous salts are not fluorescent. The photographic activity of both uranous and uranic salts was found to be proportional to their content of uranium. Becquerel also showed that preliminary stimulation by sunlight was wholly unnecessary. Uranium salts which had been kept in the dark for years were found to be just as active as those which had been recently exposed to brilliant sunlight.

The properties of the rays emitted by uranium salts differ in many respects from those of the X-rays. The rate of emission of the radiation from uranium remains unaltered

* Compt. rendus, 122, 420 (1896).

at the highest or the lowest obtainable temperatures. The entire behavior of these salts justifies the conclusion, that the continuous emission of penetrating rays is a specific property of the element uranium itself. This property of spontaneously emitting radiations capable of penetrating substances opaque to ordinary light is called *radioactivity*.

Discovery of Radium. Shortly after the discovery of the radioactivity of uranium, the element thorium and its compounds were also found to be radioactive. As a result of a systematic examination by Mme. Curie,* of minerals known to contain uranium or thorium, it was learned that many of these were much more radioactive than either uranium or thorium alone. Thus, pitchblende, one of the principal ores of uranium, was found to be four times more active than uranium alone, while chalcolite, a phosphate of copper and uranium, was found to be at least twice as active as uranium. On the other hand, when a specimen of artificial chalcolite, prepared in the laboratory from pure materials, was examined, its activity was found to be proportional to the content of uranium. Mme. Curie concluded from this result, that natural chalcolite and pitchblende must contain a minute amount of some substance much more active than uranium.

With the assistance of her husband, Mme. Curie undertook the task of separating this unknown substance from pitchblende. Pitchblende is an extremely complex mineral and its systematic chemical analysis calls for skill and patience of a high order. Without entering into details as to the analytical procedure, it must suffice here to state the results obtained. Associated with the bismuth occurring in pitchblende, a very active substance was discovered, to which Mme. Curie gave the name polonium in honor of her native land, Poland. In like manner, an extremely active substance was found associated with barium in the alkaline earth group. This substance was called radium because of its great radioactivity.

While the isolation of pure polonium is extremely difficult, and while sufficient quantities have not been obtained to permit determinations of its physical properties, the isolation of radium in relatively large amounts is readily accomplished. The pure bromides of radium and barium are prepared together, and the two salts are then separated by a series of fractional crystalliza-

* Compt. rendus, 126, 1101 (1898).

tions. That the salts of barium and radium are very similar in chemical properties, is shown by the fact that they separate together from the same solution. The atomic weight of radium has been determined by several investigators, the accepted value being 226. With the exception of uranium, radium is the heaviest element known.

In 1910, Mme. Curie* succeeded in obtaining metallic radium. It is a metal possessing a silvery luster, which dissolves in water with energetic evolution of hydrogen and tarnishes rapidly in air with the formation of the nitride.

Analysis has revealed the fact that in all of the principal uranium ores, the amounts of uranium and radium bear to each other a fixed ratio, one part of the latter being found associated with every three million two hundred thousand parts of the former. Since the amount of uranium occurring in pitchblende may vary from 1 to 50 per cent, it follows that, even with high grade ores, several tons would be required to furnish one gram of pure radium.

Ionization of Gases. The radiations emitted by radioactive substances, like the X-rays, have the power of rendering the air through which they pass conductors of electricity. To account for this action, Thomson and Rutherford formulated the theory of gaseous ionization. According to this theory, which has since been experimentally confirmed, the radiations break up the components of the gas into positive and negative carriers of electricity called *ions*.

If two parallel metal plates are connected to the terminals of a battery, and a radioactive substance is placed between them, the air will be ionized and, owing to the movement of the positive and negative ions toward the plates of opposite sign, an electric current will pass between the plates. If the electric field is weak, the mutual attraction between the positive and negative ions will cause many of them to recombine before reaching the plates, and the resulting current will be small. As the strength of the field is increased, the greater will be the speed of the ions toward the plates and the smaller will become the tendency toward recombination. Ultimately, with increasing strength of field all of the ions will be swept to the plates as fast as they are formed, and the ionization current will attain a

* Compt. rendus, 151, 523 (1910).

maximum value. This limiting or *saturation current* affords the most accurate method for the measurement of radioactivity.

The method is so sensitive that, by means of it alone, it is possible to detect amounts of radioactive products far beyond the reach of the balance, or the spectroscope. It has been found, that 0.00000002 mg. of radium can be detected with certainty.

The theory of gaseous ionization has been confirmed in several different ways, but one of the most striking verifications of the theory is that due to C. T. R. Wilson. Making use of the fact, that the ions tend to condense water vapor around themselves as nuclei, Wilson has succeeded in actually photographing the path of an ionizing ray in air.

Photographic Action of Radiations. It has already been pointed out, that the radiations from radioactive substances are capable of affecting a photographic plate. The photographic action of the radiations has been employed quite extensively in studying radioactive phenomena from a purely qualitative standpoint. The method employed, consists in exposing the photographic plate, which has previously been wrapped in opaque black paper, to the action of the radiations. The time of exposure varies with the nature of the substance under examination, a few minutes being required for highly active preparations, while several days, or even weeks, may be needed for preparations of low activity.

Phosphorescence Induced by Radiations. A screen covered with crystals of phosphorescent zinc sulphide is rendered luminous, when exposed to fairly intense radiation from a radioactive substance. This phenomenon has been shown to be due to the bombardment of the crystals of zinc sulphide by the so-called α-rays (see below). When the screen is examined with a lens, the phosphorescence is seen to consist of a series of scintillations of very short duration.

Nature of the Radiations. The ionizing, photographic and luminescent effects produced by the radiations from radioactive substances are not sufficient to differentiate them from cathode rays, or from X-rays, although each of these effects may be employed to determine the intensity of the radiations.

Evidence as to the composite character of the radiations was furnished by a study of their penetrating power, as well as by investigations of their behavior, when subjected to the action of

magnetic or electric fields. A thin sheet of aluminum, or a few centimeters of air, was found sufficient to cut off a large percentage of the rays. The unabsorbed portion of the radiation was found to consist of two distinct types, one of which was cut off by five or six millimeters of lead, while the other possessed such great penetrating power that its presence could be readily detected after passing through a layer of lead fifteen centimeters thick.

Rutherford named these three distinct types of radiation, the α-, β-, and γ-rays, respectively. The penetrating powers of the α-, β-, and γ-rays may be approximately expressed by the proportion 1:100:10,000; that is, the β-rays are 100 times more penetrating than the α-rays, while the γ-rays are 100 times more penetrating than the β-rays.

The general characteristics of the three kinds of rays may be briefly summarized as follows: —

(1) *α-Rays.* The α-rays consist of positively charged particles moving with speeds approximately one-tenth as great as that of light. These particles have been shown to be identical with helium atoms carrying two positive charges of electricity. They are appreciably deflected from a rectilinear path by magnetic and electric fields. They possess great ionizing power, but relatively little penetrating power, or photographic action. The depth to which an α-particle penetrates a homogeneous absorbing medium before losing its ionizing power, is known as its "range." The range has been found to be proportional to the cube of the initial speed of the α-particle, and is one of the characteristic properties of the radio-elements emitting α-rays.

(2) *β-Rays.* The β-rays consist of negatively charged particles moving with speeds varying from two-fifths to nine-tenths of the speed of light. They are, in fact, electrons moving with much greater speeds than those shot out from the cathode in a vacuum tube. While the α-particles emitted by a particular radio-element have a definite velocity, the corresponding β-ray emission consists of a flight of particles having widely different speeds. The penetrating power of the β-rays is conditioned by the speed of the particles, those which move most rapidly possessing the greatest penetrating power. The ionizing action of the β-rays is much weaker than that of the α-rays, while exactly the reverse is true of their photographic action.

(3) *γ-Rays.* The γ-rays are identical with X-rays. They

consist of extremely short waves of light, the wave-length varying from about 1×10^{-8} cm., for the rays of low penetrating power, to about 1×10^{-9} cm., for the most penetrating rays. Obviously, γ-rays cannot be deflected from a rectilinear path by either electric or magnetic fields.

The Radium Emanation (Radon). When a specimen of radium bromide is gently heated, or when a current of air is bubbled through a solution of a radium salt, a small volume of an exceedingly radioactive gas is obtained. Rutherford, to whom we are indebted for much of our knowledge of this interesting substance, named it, somewhat vaguely, the "emanation." In 1911, Ramsay and Gray,* making use of a special quartz micro-balance, sensitive to one millionth of a milligram, succeeded in determining the mass of a known volume of pure emanation. On the assumption that the gas is monatomic, they computed the average value of its atomic weight to be 222. The value of the atomic weight of the emanation, taken together with its chemical inertness, served to determine its position in the group of non-valent elements in the periodic table. In order to emphasize its relationship to the inert gases the International Committee on Chemical Elements proposed that it be named "radon."

The following crucial experiment, carried out by Rutherford and Royds,† with radon, furnished conclusive evidence that the α-particle consists of an atom of helium carrying two positive charges. A glass bulb was blown with walls thin enough to permit the passage of the α-particles, but of sufficient strength to withstand atmospheric pressure. The bulb was filled with radon under pressure, and then enclosed in an outer glass tube, to which a spectrum tube had been sealed. On exhausting the outer tube, and examining the spectrum of the residual gas, no evidence of helium was obtained until after an interval of twenty-four hours. After four days, the yellow and green lines characteristic of helium were plainly visible, while at the end of the sixth day, the complete spectrum of the element was obtained. The unavoidable conclusion from this experiment is, that the presence of helium in the outer tube must have been due to the α-particles which were projected through the thin walls of the inner tube. In another experiment, the inner tube was filled with pure helium under pressure, while the

* Proc. Roy. Soc. A **84**, 536 (1911).

† Phil. Mag., VI, **17**, 281 (1909).

exhausted outer tube was examined for helium. No trace of the gas could be detected spectroscopically, even after an interval of several days, thus proving that the helium detected in the first experiment must have resulted from the α-particles which had been shot out from the radon with sufficient energy to penetrate the thin walls of the inner tube. These experiments leave no room for doubt, that an α-particle becomes a helium atom when its positive charge is neutralized.

There is an abundance of experimental evidence which proves that only one α-particle is expelled from each atom of radium in the formation of radon. The process may be represented by the equation,

$$\text{Ra} - \text{He} = \text{Rn}.$$

Since the atomic weight of radium is 226, and that of helium is 4, it follows, that the atomic weight of radon should be 222. This, it will be remembered, is exactly the value which Ramsay and Gray obtained for the atomic weight of radon.

Taken mass for mass, radon is much more radioactive than the radium from which it was derived, but the activity is found to diminish rapidly with time, and practically to have disappeared at the end of a month.

A radium salt loses the greater part of its activity on de-emanating, but if it is examined from day to day, it will be found to be recovering its activity at precisely the same rate as the radon, which was derived from it, loses its activity. In other words, when the processes of decay and recovery are examined quantitatively, it is found that they are complementary, and that the total radioactivity remains unaltered. The two processes of decay and recovery follow an exponential law which is expressed by the following equations:

$$I_t = I_0 e^{-\lambda t}, \qquad \text{(decay)} \qquad (1)$$

and

$$I_t = I_0 (1 - e^{-\lambda t}), \quad \text{(recovery)} \qquad (2)$$

where I_0 is the initial activity, I_t the activity after a time t, λ a constant, known as the *radioactive constant*, and e the base of the natural system of logarithms. The decay curve of radon, and the recovery curve of the activity of radium, as measured by the α-rays, are shown in Fig. 173. From these curves, it will be ap-

parent that while the radon is decaying from day to day, the radium is in turn producing a fresh supply. This behavior is typical of all radioactive bodies and illustrates the law of the "conservation of radioactivity."

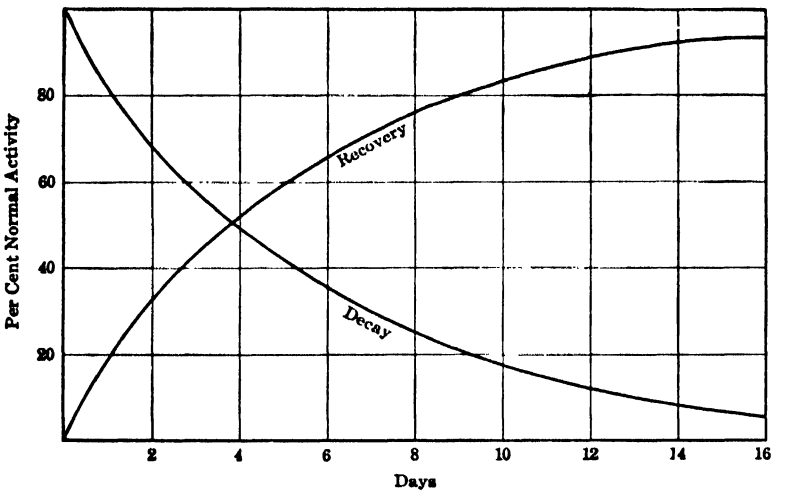


Fig. 173

Counting the α-Particles. Rutherford and Geiger * devised an electrical method for counting the α-particles. In their experiment the source of the α-particles was a small disc which had been exposed to the radium emanation for some hours. This disc was placed in an evacuated tube, at a measured distance from a small aperture of known cross-section. The aperture was closed with a thin plate of mica through which the α-particles could pass with ease. After passing through the mica plate, the α-particles entered an ionization chamber filled with air at reduced pressure, and fitted with two charged metal plates connected with appropriate apparatus for measuring ionization currents. Whenever an α-particle entered the ionization chamber, a momentary current passed, producing a sudden deflection of the needle of the electrometer. By counting the number of throws of the needle occurring in a definite interval of time, the total number of α-particles passing through the ionization chamber could be determined. Knowing the distance of the source of the radiations from the

* Proc. Roy. Soc. *A*, 81, 141 (1908).

aperture, together with the area of the aperture, the total number of α-particles emitted by the radioactive disc, in a given time, could be computed. Rutherford and Geiger thus found, that 1 gram of radium emits very nearly 3.4×10^{10} α-particles per second. Having determined the total number of α-particles emitted, it only remained to measure the total charge, in order to calculate the charge carried by a single α-particle. From a series of very consistent measurements, the charge carried by a single α-particle was found to be 9.3×10^{-10} electrostatic units. Since the fundamental charge, e, has been shown to be 4.89×10^{-10} electrostatic units, it follows that the α-particle carries two positive charges of electricity.

Avogadro's Constant from Radioactive Data. The rate at which helium is produced by radium has been very carefully determined by Rutherford and Boltwood,* who found it to be 0.107 cu. mm. per day per gram of radium. Since it has been established that one gram of radium emits 3.4×10^{10} α-particles per second, it follows that the value of Avogadro's constant is 6.16×10^{23}. (Let the student verify this.) It will be seen, that this result agrees well with the value previously found for this constant from entirely different experimental data.

The Disintegration Theory. The processes involved in the transformation of the radio-elements are very different in character from those occurring in ordinary chemical reactions. Thus, it has not been found possible to alter, by any known means, the rate at which the radio-elements undergo change. Whatever hypothesis is advanced to account for the phenomena of radioactivity, it must offer not only a satisfactory explanation of the production of a series of active elements, differing from each other and from the parent element, in both physical and chemical properties, but also it must account for the enormous development of energy which invariably accompanies these transformations.

The theory of "atomic disintegration," advanced by Rutherford and Soddy, in 1903, has shown itself capable, not only of interpreting the extremely complex known facts of radioactivity, but also of predicting and explaining many new ones. According to this theory, the atoms of the radio-elements are assumed to undergo spontaneous disintegration, each atom passing through a series of well-defined changes accompanied, in most cases, by

* Phil. Mag. 22, 586 (1911).

the emission of α-particles.* It is supposed that, on the average, a definite proportion of the atoms of each radio-element becomes unstable at a given time and, as a result of this instability, an α-particle is expelled with great velocity. The expulsion of an α-particle leaves the new system four units lighter than the original one, and possessing quite different physical and chemical properties. This new system, in turn, becomes unstable and expels another α-particle, with the simultaneous production of a still lighter system. The process of disintegration, once begun, proceeds successively from one radio-element to the next, each transformation taking place at a definite, measurable rate, until ultimately, a stable system is produced and further disintegration ceases.

It has already been pointed out, that a radio-element decays exponentially with time according to the equation:

$$I_t = I_0 e^{-\lambda t},$$

In this equation, the radioactive constant represents the fraction of the total amount of radioactive substance undergoing disintegration in a unit of time, provided the latter is so small that the quantity at the end of the time unit is only slightly different from the initial quantity. The reciprocal of the radioactive constant is called the *average life* of the element. Soddy defines the average life of a radio-element as "the sum of the separate periods of future existence of all the individual atoms, divided by the number in existence at the starting point." If n_t represents the number of atoms of a radio-element changing in unit time, at the end of a time t, and n_0, the corresponding value when $t = 0$, equation (1) may be written,

$$n_t = n_0 e^{-\lambda t}. \tag{3}$$

In order to determine the initial rate of change, let N_0 denote the total number of atoms originally present, and N_t the number remaining unchanged at time t; then we have,

$$N_t = \int_t^\infty n_t dt = \frac{n_0}{\lambda} e^{-\lambda t}. \tag{4}$$

But when $t = 0$, $N_0 = N_t$,

and
$$N_0 = \frac{n_0}{\lambda}. \tag{5}$$

Hence
$$N_t = N_0 e^{-\lambda t}.$$

* The emission of a β-particle produces no appreciable change in weight.

On differentiating, we have

$$\frac{dN}{dt} = -\lambda N. \tag{6}$$

Or, stated in words, the rate at which the atoms of a radio-element undergo disintegration at any given time is proportional to the total number in existence at that time.

This law of radioactive change is also peculiar to unimolecular chemical reactions (see p. 427). The velocity of a unimolecular reaction, however, is conditioned by the temperature, whereas the velocity of a radioactive change remains unaltered at the highest and the lowest attainable temperatures.

The time required for one-half of a radio-element to undergo transformation is known as the *period of half change*, T, and may be readily calculated from λ, as follows,

$$\log 2 = 0.4343\ \lambda T,$$

or

$$T = \frac{0.6932}{\lambda}.$$

Radioactive Equilibrium. It is evident, that a state of equilibrium must ultimately be attained among the atoms of a radioactive substance. When the rate of production of a radio-element from its parent element is equal to its rate of disintegration into the next succeeding element of the series, the substance is said to be in *radioactive equilibrium*. The principle of radioactive equilibrium may be illustrated by the disintegration of radium into radon. Owing to the rapidity with which radon disintegrates, it does not accumulate continuously, but reaches a definite equilibrium ratio with respect to its parent, radium, in which the amount of radon disappearing is just counter-balanced by the amount of fresh radon formed. If λ_1 is the radioactive constant of radium, and N_1 is the total number of radium atoms involved, then the number of radium atoms undergoing disintegration into radon per second is $\lambda_1 N_1$. But when equilibrium is attained, $\lambda_1 N_1$ must be equal to the number of radon atoms disappearing. If λ_2 is the radioactive constant of radon, and the number of atoms of radon present during equilibrium is N_2, the number of atoms of radon disintegrating per second is $\lambda_2 N_2$. Therefore, we have

$$\lambda_1 N_1 = \lambda_2 N_2$$

or

$$N_2/N_1 = \lambda_1/\lambda_2 \tag{7}$$

This mathematical expression of the most important law of radioactive change, may be translated into words as follows: — In successive disintegrations, each product accumulates until a fixed ratio with respect to the parent element is attained, and this ratio is inversely proportional to the respective radioactive constants of the two elements, or, is directly proportional to their respective average lives. In order that this law may hold rigidly, it is necessary that the period of the parent element should be appreciably longer than the periods of any of its products. Where this is the case, the product chosen need not be the next in succession, but may be any one of the successive elements in the series.

It is evident, that the amount of radon in equilibrium with one gram of pure radium is a definite quantity. At the Radiology Congress held in Brussels, in 1910, it was decided that this equilibrium quantity of radon should be called the "*curie*," in honor of M. and Mme. Curie. The volume of radon from one gram of radium can be calculated from a knowledge of the number of α-particles expelled from one gram of radium in one second. It has already been stated, that this number is 3.4×10^{10}. Since each radium atom, after the expulsion of an α-particle, becomes an atom of radon, it follows that the number of atoms of radon, q, formed per gram per second is 3.4×10^{10}. When equilibrium is attained, the number of atoms of radon, N, present per gram will be $N = q/\lambda$. Since $\lambda = 2.085 \times 10^{-6}$ per second, we have $N = 1.63 \times 10^{16}$. Since there are 2.75×10^{19} molecules present in one cubic centimeter of any gas, under standard conditions of temperature and pressure, the volume of one curie of radon will be 0.59 cubic millimeter. Rutherford found, by direct experiment, 0.6 cubic millimeter as the volume of one curie of radon, which is in remarkably close agreement with the calculated value. Since a curie is a relatively large unit in comparison with the amounts of radon ordinarily obtainable, it is convenient to use as a practical unit, the milli-curie, which is, as its name implies, the amount of radon in equilibrium with ten milligrams of pure radium.

The Origin of Radium and the Uranium Disintegration Series. As the result of a large amount of careful experimental work, it has been shown that radium is but one of a series of radio-elements, each of which is formed by the atomic disintegration of the pre-

ceding member of the series, in precisely the same manner as radon is formed from radium.

Very soon after the discovery of radium, it was suspected that some intimate connection might be found to exist between radium and uranium, but it was not until after Strutt and Boltwood, from an examination of a large number of uranium-bearing minerals, had established the existence of a constant ratio between the percentages of uranium and radium, that this suspicion was confirmed.

Radium is not the direct product of uranium, but rather is the fifth successive member of the disintegration series which has its origin in uranium. Uranium changes into UX_1, with the simultaneous expulsion of an α-particle and a consequent loss of four units in atomic weight. The element uranium disintegrates at an exceedingly slow rate, the probable value of its average life being 8,000,000,000 years. The element UX_1 changes with the emission of a β-particle, and hence without loss of weight, into the element UX_2 which, because of its brief average life of 1.65 minutes, is sometimes called brevium. Two other radio-elements, UII and Io, with periods of average life of 3,000,000 and 100,000 years respectively, are formed in succession from UX_2 before the element radium is formed from ionium. Since three α-particles are expelled in the course of the five successive disintegrations involved in the production of radium from uranium, it follows, that the atomic weight of radium should be $3 \times 4 = 12$ units lighter than the atomic weight of uranium, or $238 - 12 = 226$. It will be seen, that the experimentally determined value of the atomic weight of radium agrees perfectly with that predicted from the disintegration theory.

If a negatively charged wire be introduced into a vessel containing radon, an extremely radioactive substance, known as the "active deposit," is condensed upon its surface. This deposit, which can be detected by neither balance nor microscope, has been found to consist of the successive disintegration products of radon. The atomic disintegration of radon takes place in eight distinct successive stages, the first four radio-elements of the active deposit being characterized by very short average lives, ranging from 38.5 minutes for RaB, to one-millionth of a second for RaC′, while the remaining elements of the series undergo transformation at a much slower rate, their average lives varying from

7.25 days to 24 years. It is of interest to note, that RaF has been found to be identical with polonium, the first radio-element to be isolated from pitchblende by Mme. Curie.

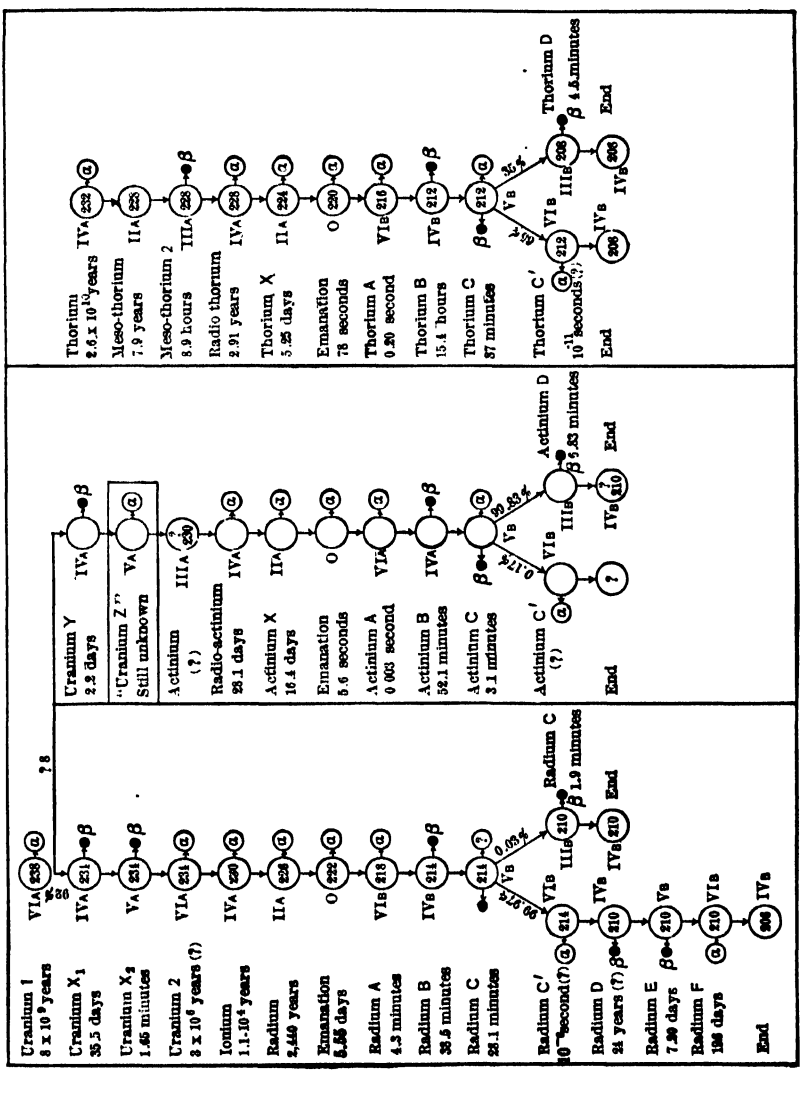
While lack of space precludes a detailed consideration of thorium and actinium, it should be mentioned that each of these elements disintegrates in a similar manner to uranium, giving rise to a series of interesting radio-elements which, in general, are shorter lived than the members of the uranium series. Taking the three series together, the science of radioactivity now embraces nearly forty elements each of which is endowed with specific properties and with periods of existence varying from thousands of millions of years on the one hand, to a small fraction of a second on the other. Soddy says of the radio-elements, "It is unlikely that any more of these unstable elements remain to be discovered, unless some entirely unknown and unsuspected source of radioactive materials is found." The table shown on p. 679 gives the three disintegration series as arranged by Soddy.

The numbers within the circles denote the atomic weights of the elements, while the small circles and dots at the right of the larger circles indicate the character of the radiation given out at each stage of the disintegration process. The average life, $1/\lambda$, of each element in the series is given below the name of the element.

The Ultimate Product of Radioactive Change. It will be observed that the end-product of the uranium series is an inactive element, having an estimated atomic weight of 206. If this is really an inactive product, and not an element, which is undergoing transformation at such an excessively slow rate as to be beyond the reach of our present experimental methods, it follows that the element must have been continuously accumulating in all of the minerals containing uranium since their original formation, and furthermore, that it must be one of the more common elements. Such an element is lead, which not only is found in all of the uranium minerals, with the exception of autunite, but also is present in amounts which are proportional to the age of the geological formation from which the mineral is obtained. There is an abundance of indirect evidence which makes it appear highly probable, that the ultimate product of the disintegration of uranium is an isotopic form of lead. It is hoped, however, that direct evidence on this question may soon be forthcoming, since Mme.

Curie and Dr. Debierne have undertaken the separation of a large amount of polonium from pitchblende, with a view to proving, by the aid of the spectroscope, that the disintegration product of polonium is really lead.

TABLE SHOWING DISINTEGRATION SERIES



The estimated atomic weights of the end-products of the other two series are 206 or 210, in the case of the actinium series, and 208, in the case of the thorium series. These values suggest the possibility that the ultimate products of these series also may be isotopic forms of lead. The evidence, however, in the case of thorium is far less definite than in that of uranium, while in the case of actinium, it may be said, that in the absence of definite knowledge of its atomic weight or that of any of its disintegration products, deduction of the atomic weight of the end-product of the series is hardly justifiable.

The atomic weight of lead, obtained from radioactive minerals collected at widely different points, has been determined with extreme accuracy by Richards and his co-workers.* As the following table shows, all of the values of the atomic weights are less than 207.20, the value recently found by Baxter and Grover,† as a result of their precise determinations of the atomic weight of inactive lead obtained from various sources.

ATOMIC WEIGHT OF LEAD OF RADIOACTIVE ORIGIN

Source	Atomic Weight
North Carolina uraninite	206.40
Joachimsthal pitchblende	206.57
Colorado carnotite	206.59
Ceylon thorianite	206.82
English pitchblende	206.86
Australian carnotite	206.34
Norwegian cleveite	206.08
Ordinary lead	207.20

Notwithstanding the variation in the values of the atomic weight of lead derived from radioactive sources, the ultra-violet spectra of the different specimens have been shown to be identical with the spectrum of ordinary inactive lead. About one kilogram of lead from a radioactive source was converted by Richards and Hall‡ into the nitrate, which was then subjected to a series of fractional

* Jour. Am. Chem. Soc. **36**, 1329 (1914); **38**, 1658, 2613 (1916); **40**, 1409 (1918).

† Ibid. **37**, 1058 (1915).

‡ Jour. Am. Chem. Soc. **39**, 531 (1917).

crystallizations with a view to effecting a possible separation of isotopic forms. Notwithstanding the fact, that over one thousand crystallizations were performed, no indication was obtained of any separation having been brought about. Not only are the solubilities of the isotopic nitrates identical, but also their spectra and refractive indices are likewise the same.

Total Energy Evolved by the Complete Disintegration of Radium. Curie and Laborde* were the first to call attention to the interesting fact, that the temperature of radium compounds was uniformly higher than that of their environment. Careful measurements have shown that one gram of radium evolves heat at the rate of approximately 133 gram-calories per hour. A knowledge of this constant, together with the value of the average life of radium, enables us to calculate the total number of calories of heat energy which will be evolved in the course of the complete disintegration of a given mass of radium. Thus, the energy evolved by one gram of radium during its complete disintegration is computed as follows: — since there are 8,760 hours in one year, one gram of radium will evolve $133 \times 8{,}760 = 1{,}160{,}000$ calories per year, and since the average life of radium is 2,440 years, the total energy evolved in its disintegration will be $1{,}160{,}000 \times 2{,}440 = 2{,}830{,}400{,}000$ calories. To give some idea of the significance of these figures, it may be stated that this amount of energy is equivalent to one million times the amount of heat developed in the combustion of an equal weight of high-grade coal.

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* Compt. rendus, **136**, 673 (1903).

CHAPTER XXII

ATOMIC STRUCTURE

The Modern Conception of Atomic Structure. From the establishment of the atomic theory on an experimental basis, by Dalton in 1808, until the closing years of the nineteenth century, the accumulated experience of chemists had confirmed the correctness of Dalton's hypothesis and had firmly settled the conviction that atoms could not be disintegrated through the application of any chemical or physical agency known to man. During the last twenty-five years, however, largely as a result of the discovery of radioactivity and the remarkable advances in knowledge in the realm of the electron, it has become necessary to modify our earlier views both as to the indivisibility and the permanence of atoms.

According to the modern theory of the constitution of matter, it is believed that the atoms of the different elements all possess the same general type of structure. At the center of the atom there is a minute, positively charged nucleus, surrounded by a miniature solar system of electrons. The investigations of Rutherford and Geiger * show, that the character of the deflection of α-particles shot out from radioactive atoms at speeds approximating 20,000 miles per second, and consequently completely penetrating other atoms, is such as to indicate an extremely high concentration of positive electricity on the central nucleus. The central nucleus, which is supposed to represent nearly the entire mass of the atom, is thought to be very small in comparison with the size of the atom as a whole. Recent investigations make it appear probable, that the maximum diameter of the nucleus of the hydrogen atom is about one one-hundred-thousandth of the diameter commonly attributed to the atom. In commenting on this statement, Harkins says: — † "On this basis the atom would have a volume a million-billion times larger than that of its nucleus, and thus the nucleus of the atom is much smaller in comparison with the size

* Phil. Mag., 21, 669 (1911).

† Science, 66, 419 (1917).

of the atom than is the sun when compared with the dimensions of its planetary system." It is highly probable that the central nucleus is itself made up of a definite number of units of positive electricity, together with a small number of attendant electrons.

It is further assumed that the units of positive electricity are hydrogen atoms, each of which has been deprived of one electron. The hydrogen nucleus is more commonly known as the "proton." If the mass of an atom is largely due to the presence of hydrogen nuclei, then we should expect Prout's hypothesis to hold, and the atomic weights of the elements to be exact multiples of the atomic weight of hydrogen. When we consider, however, that according to the electromagnetic theory, the total mass of a body composed of positive and negative units is dependent upon the relative positions of these units when packed together, it is evident, that the mass of the atom will not necessarily be an exact multiple of the mass of the hydrogen atom.

It has already been pointed out, that helium is a product of many radioactive transformations. This fact may be taken as an indication of the extraordinary stability of the helium atom. Because of its stability, the nucleus of this atom has come to be considered as a secondary unit of positive electricity. The nucleus of the helium atom, or the nucleus of an α-particle is assumed to consist of four hydrogen nuclei with two nuclear electrons.

In a recent address, Rutherford * says:—

"This minute but massive nucleus is, in a sense, a world of its own which is little, if at all, influenced by the ordinary physical and chemical forces at our command. In many respects, the problem of nuclear structure is much more difficult than the corresponding problem of the arrangement and motions of the planetary electrons, where we have a wealth of available information, both physical and chemical, to test the adequacy of our theories. The facts known about the nucleus are few in number and the methods of attack to throw light on its structure are limited in scope."

The configurations of the planetary electrons determine the physical and chemical properties of the different elements, while their orbital motions are responsible for the characteristic X-ray and optical spectra of the elements. On the other hand, the phenomena of radioactivity and all other properties which are de-

* Rutherford, address on "The Natural and Artificial Disintegration of the Elements," on the occasion of the Franklin Institute Centenary Celebration, Sept., 1924.

pendent on the mass of the atom are determined by the nucleus alone.

The Atomic Number. Since the algebraic sum of the positive and negative electrification on an atom must be zero, it follows, that the excess positive charges resident upon the nucleus must be equal to the number of electrons outside the nucleus. If the number of outer electrons is N, the total nuclear charge will be Ne, where e is the charge on a single electron. This number N, known as the *atomic number*, is now regarded as more important and characteristic than the atomic weight. Thus, when the elements are arranged in the order of their atomic numbers, rather than in the order of their atomic weights, the inconsistencies which have previously been pointed out in connection with the positions of argon and potassium, of iodine and tellurium, and of nickel and cobalt in the periodic table, entirely disappear. In fact, it is now recognized that the order of the periodic system is intimately connected with the atomic structure of the elements.

X-Rays and Atomic Structure. The discovery by W. L. Bragg, in 1912, that X-rays undergo reflection at crystal surfaces, and the subsequent development by Mr. Bragg and his father, W. H. Bragg, of the X-ray spectrometer, has led to a series of investigations of the utmost importance to both the chemist and the physicist.

The bombardment of metal plates, usually of platinum, by electrons gives rise to X-rays. The radiation issuing from an X-ray tube is very far from homogeneous. It has been found, however, that every substance, when properly stimulated, is capable of emitting a homogeneous and characteristic X-radiation, the penetrating power of which is wholly determined by the nature of the elements of which the substance is composed. The penetrating power of this typical X-radiation increases with the atomic weight of the radiating element. With elements whose atomic weights are less than 24, the radiation is too feeble to be easily measured. It is important to note, that this property of the elements is not a periodic function of the atomic weight. This type of X-radiation is entirely independent of external conditions, indicating that it is closely connected with the internal structure of the atoms from which it emanates.

By making use of the reflecting power of one of the cleavage planes of a crystal, and employing different metals as anti-cath-

odes in an X-ray tube, Moseley * succeeded in photographing the X-ray spectra, characteristic of a number of the elements. He found a regular recurrence of certain groups of lines in the X-ray spectra of a number of elements occupying successive positions in the periodic table. These series of lines in the different spectra bore a striking resemblance to each other, both as to their relative positions and their individual intensities. In fact, the only marked difference between the spectra of the different elements was in the wave-lengths of their characteristic lines. With increasing atomic number the entire series of lines constituting the spectra of the elements was found to undergo a gradual shift in the direction of shorter wave-lengths. Furthermore, the elements of higher atomic numbers were found to give two new series of characteristic lines of longer wave-length, and these also underwent a displacement in the direction of shorter wave-lengths as the atomic number of the element increased. These three series of lines have been designated the "K," "L," and "M" series, respectively.

The K series consists of five lines and has been observed from sodium to neodymium; the L series, of ten to fourteen lines, has been observed from zinc to uranium, while the M series, consisting of seven lines, has been observed from gold to uranium.

Moseley discovered that a very simple numerical relationship exists between the frequency of corresponding lines in the X-ray spectra of different elements and their atomic numbers. This relationship may be expressed by the equation

$$\sqrt{\nu} = A(N - b), \tag{1}$$

where ν is the frequency and N the atomic number of the element, and where A and b are constants. From equation (1) it is evident that the square root of the characteristic frequency is a linear function of the atomic number. This law, which has been found to hold equally well for the K, L and M series, is known as "Moseley's Law of High Frequency Spectra."

It has been shown by Duane,† that, for the elements from cerium to magnesium, the square root of the frequency, ν, is not quite a linear function of the atomic number, N. The relation between the square roots of the frequencies and the atomic num-

* Phil. Mag., 26, 210 (1913); 27, 703 (1914).

† Phys. Rev., 14, 516 (1919).

bers of the elements for the K, L and M series is shown graphically in Fig. 174.

In reviewing Moseley's work on X-ray spectra, Soddy* says: — "A veritable roll-call of the elements has been made by this method. Thirty-nine elements, with atomic weights between those of aluminium and gold, have been examined in this way, and in every case, the lines of the X-ray spectrum have been found to be simply connected with the integer that represents the place assigned to it by chemists in the periodic table."

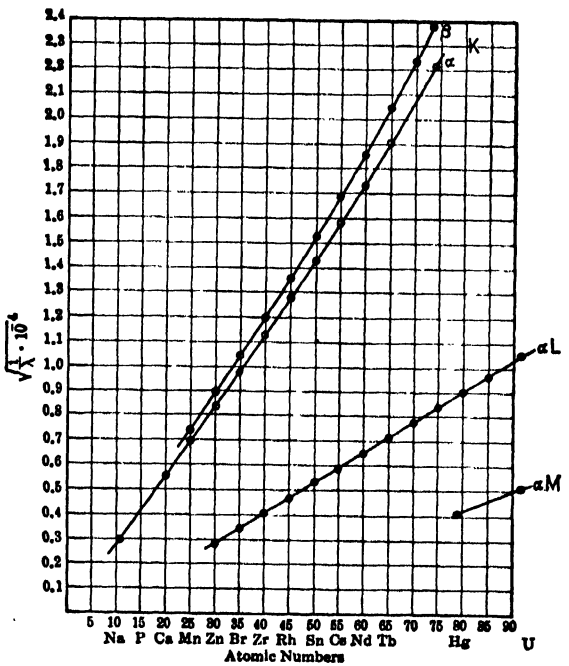


Fig. 174

One of the most interesting results of this "roll-call" of the elements is the fixing of the number of possible rare-earth elements. Between barium and tantalum there are places for only fifteen rare-earth elements and fourteen of these places are filled.† While future investigation may necessitate some rearrangement in the

* Ann. Reports on the Prog. of Chemistry, p. 278 (1914).

† Since this paragraph was written element No. 61 has been discovered by Hopkins and named by him Illinium. See Jour. Am. Chem. Soc., 48, 1585 (1926).

order of tabulation, the total number of these elements is limited to fifteen.

Periodicity among the Radio-elements. The problem of placing the newly discovered radio-elements in the periodic table remained unsolved until 1913, when Fajans* and Soddy,† working independently, discovered an important generalization concerning the changes in chemical properties resulting from the expulsion of α- and β-particles during radioactive transformations. This important generalization may be stated as follows: — *The expulsion of an α-particle causes a radioactive element to shift its position in the periodic table two places in the direction of decreasing atomic weight, whereas the emission of a β-particle causes a shift of one place in the opposite direction.* This generalization not only agrees with our present theory of atomic structure, but may be shown to be a necessary consequence of this theory.

The loss of an α-particle, or helium atom, involves a loss of 4 units in atomic weight and of 2 units of positive electricity from the nucleus of the atom. In consequence of this loss, the atomic number is diminished by 2 units, and the resulting new element will find a place in the periodic table two groups to the left of that occupied by the parent element. On the contrary, while the expulsion of a β-particle, or electron, involves practically no change in mass, the nucleus of the parent atom suffers a loss of 1 unit of negative electricity. This loss is equivalent to a gain of 1 unit of positive electricity, or to an increase of 1 unit in the atomic number, and in consequence, the position of the new element in the periodic table will be shifted one group to the right of that occupied by the parent element, with a corresponding change in valence.

Soddy's arrangement of all of the radio-elements in accordance with this generalization is shown in Fig. 175. Thus, starting with the element uranium in Group VIA, we may follow the successive steps in the radium disintegration series which was discussed in the preceding chapter. The element UX_1, resulting from U by the loss of an α-particle, is placed in Group IVA. This element in turn undergoes a β-ray change, producing the element UX_2, which is accordingly placed in Group VA. The element UII in Group VIA is formed from UX_2 by β-ray disintegration, while the element Io results from the loss of an α-particle by UII_0 with a con-

* Physikal. Zeit., 14, 49 (1913). † Chem. News, 107, 97 (1913).

sequent shift to the left into Group IVA. A similar loss of an α-particle by Io brings us to the element Ra, in Group IIA. In the successive steps of this disintegration from U to Ra, three α-particles, or 12 units of atomic mass, are lost and the atomic weight of Ra, as calculated from that of U, agrees with the atomic weight found by direct experiment. In like manner, the remaining stages of the disintegration may be followed to the end-product in Group IVB.

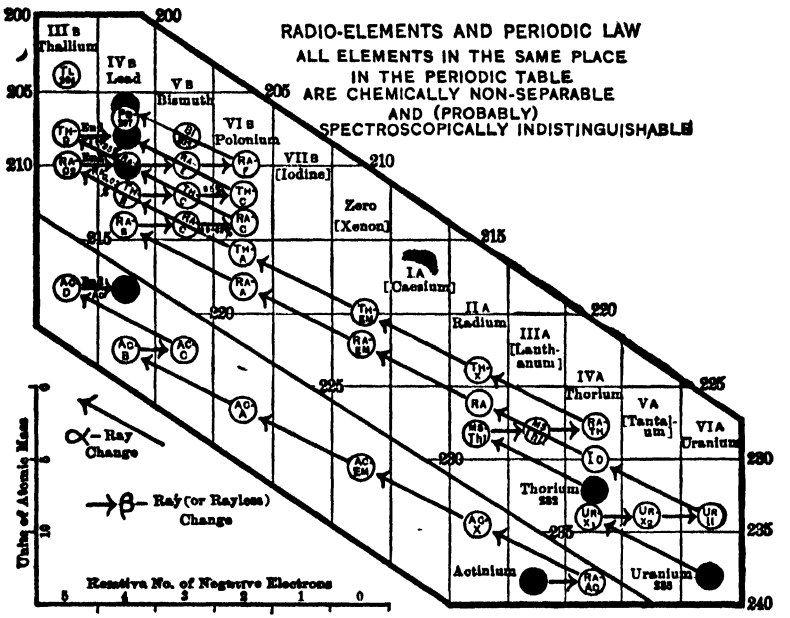


Fig. 175

Isotopes and Isobares. Perhaps the most striking feature in the table is the occurrence of several different elements in the same place, as for example in Group IVB, where in the place occupied by the element Pb, we also find RaB, RaD, ThB, and AcB, together with four other elements to which no names have been assigned, but which are none the less stable end-products. The individual members of such a group of elements occupying the same place in the periodic table, and being in consequence chemically identical, are therefore isotopic.

Just as it is possible to have elements with identical chemical properties but differing in atomic weight, so it is also possible to

have elements possessing different chemical properties with the same atomic weight. Such elements have been called by Stewart,* *isobares*. The product of a radioactive change in which a β-particle is lost is an isobare of the parent element, since its position in the periodic table has been shifted without undergoing appreciable change in mass, while its chemical properties have changed to correspond with its new position in the table. It is worthy of note, that no isobare has yet been discovered among the elements which are not radioactive.

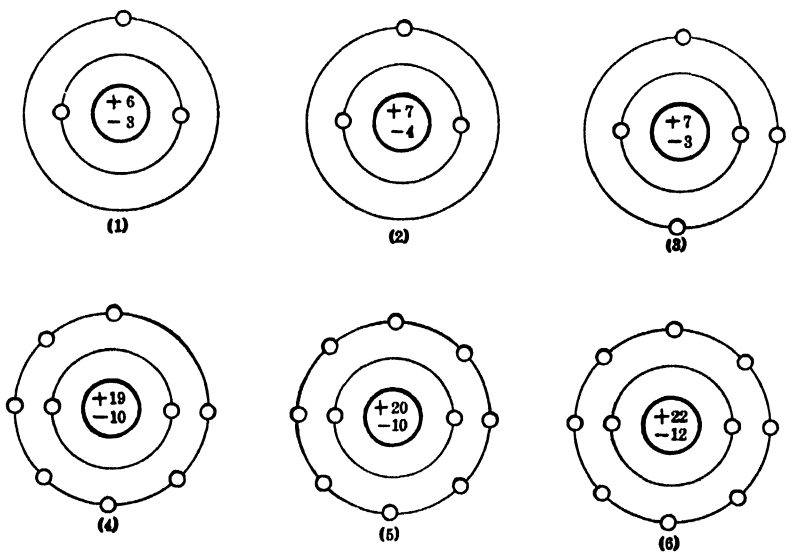


Fig. 176

It is also interesting to note in Soddy's table (Fig. 175), that "the ten occupied spaces (groups) contain nearly forty distinct elements, whereas if chemical analysis alone had been available for their recognition, only ten elements could have been distinguished."

A diagrammatic representation of the hypothetical arrangement of the electrons and protons in atoms, as suggested by Aston, will help to make clear the distinction between isotopes and isobares. In Fig. 176, the small dark circles represent the nuclei of atoms, the number of protons and electrons comprising them being indicated by the positive and negative numerals, respectively. The

* Phil. Mag., 36, 326 (1918).

outer, or planetary, electrons are represented by the smaller circles. Diagram (1) represents an element of atomic weight 6. Since its nucleus is made up of six protons and three electrons, its atomic number must be 3. Therefore, it represents the lighter isotope of lithium whose atomic weight is 6, or Li^6. In order that the atom may preserve its electrical neutrality, there must be three planetary electrons. If now one electron and one proton be added to the nucleus of the atom represented in (1), we get the arrangement represented in (2). But since the total nuclear charge remains unchanged, the electrical neutrality of the atom is undisturbed and the number of planetary electrons remains as in (1). It follows, therefore, that all of the properties of the atom which depend upon the number of external electrons will remain unaltered, and the only difference between (1) and (2) will be a difference of one unit in atomic weight. The atoms represented by (1) and (2), therefore, are isotopes, the lighter being Li^6 and the heavier Li^7. Again, let one proton and one electron be added to (1), but instead of letting both enter the nucleus, as before, let the proton enter the nucleus and the electron enter the outer orbit, as indicated in (3). We now have a nuclear charge of +4 and two electrons in the outer orbit. In this case the properties will differ markedly from those of the element lithium, but will be identical with the properties of the element beryllium with which it will be isotopic. The atomic weight of (3), however, will be seen to be the same as that of (2), and, therefore, (2) and (3) must be isobares. In like manner, the configuration indicated in (4) will be seen to represent the atom of fluorine, while (5) and (6) represent the two isotopes of neon, Ne^{20} and Ne^{22}.

The Periodic Table of Harkins. In the light of recent discoveries the periodic law acquires new significance; in fact, today the periodic law may be regarded as the most comprehensive generalization in the whole science of chemistry.

While the later periodic tables are more complete than the original, owing in part to the discovery of new elements, it must be admitted, nevertheless, that relatively little real progress has been made, until recently, toward removing the seemingly inherent defects of the system.

A satisfactory periodic table should meet the following requirements:

(1) It should afford a place for isotopic elements, such as lead.

(2) The radio-elements, together with their α- and β-disintegration products, should be shown.

(3) It should contain no vacant spaces, except those corresponding to the atomic numbers of undiscovered elements.

(4) It should bring out the relation between the elements constituting a main group, and those forming the corresponding subgroup. For example, the relation between the elements Be, Mg, Ca, Sr, Ba, and Ra, on the one hand, and the elements Zn, Cd, and Hg, on the other, should be emphasized.

(5) The elements of Group O and Group VIII should fit naturally in the table.

(6) All of the foregoing conditions should be shown by means of a continuous curve connecting the elements in the order of their *atomic numbers*, the latter having been shown to be more characteristic of an element than its atomic weight.

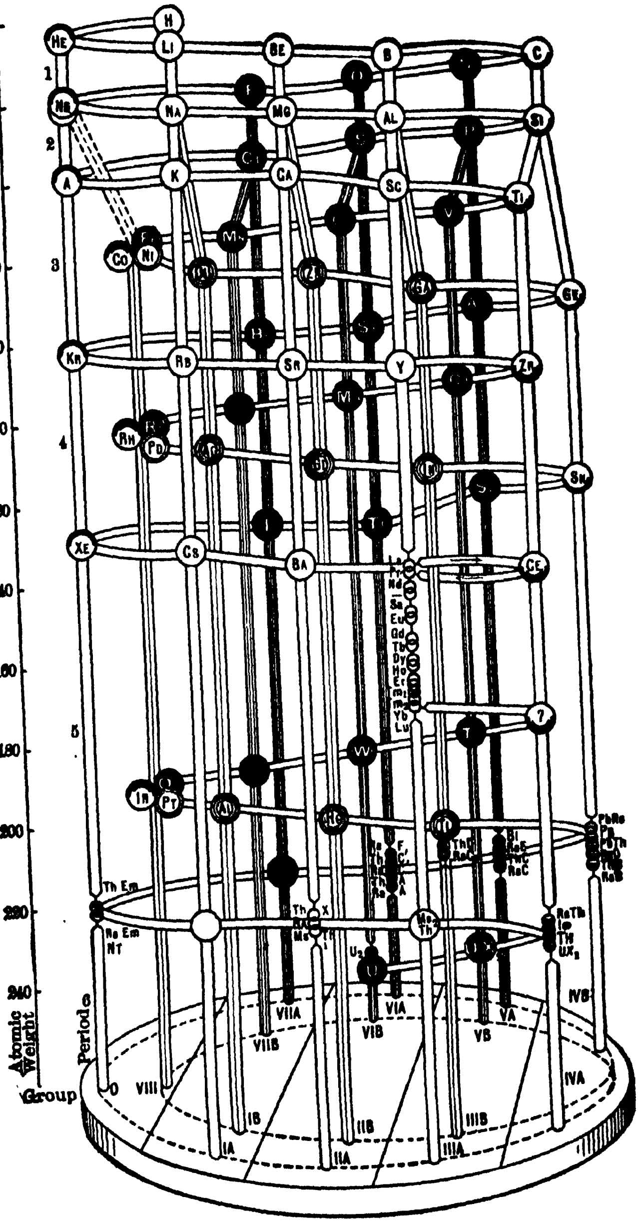
A table which satisfactorily meets these requirements has recently been devised by Harkins and Hall. This table may be constructed in the form of a helix in space, or as a spiral in a plane. The following description of the helical arrangement, shown in Fig. 177, is taken verbatim from the original paper of Harkins and Hall.*

"The atomic weights are plotted from the top down, one unit of atomic weight being represented by one centimeter, so the model is about two and one-half meters high. . . .

"The balls representing the elements are supposed to be strung on vertical rods. All of the elements on one vertical rod belong to one group, have on the whole the same maximum valence, and are represented by the same *color*. The group numbers are given at the bottom of the rods. On the outer cylinder the electro-negative elements are represented by black circles at the back of the cylinder, and electro-positive elements by white circles on the front of the cylinder. The transition elements of the zero and fourth groups are represented by circles which are half black and half white. The inner loop elements are intermediate in their properties. Elements on the back of the inner loop are shown as heavily shaded circles, while those on the front are shaded only slightly.

"In order to understand the table it may be well to take an

* Jour. Am. Chem. Soc., 38, 169 (1916).



Atomic Weight
Period
Group
0
20
40
60
80
100
120
140
160
180
200
220
240
1
2
3
4
5
6
H
HE
LI
BE
B
C
NE
NA
MG
AL
SI
A
K
CA
SC
TI
CO
NI
GA
GE
KR
RB
SR
Y
ZR
RH
PD
SN
XE
CS
BA
CE
La
Pr
Nd
Sa
Eu
Gd
Tb
Dy
Ho
Er
Yb
Lu
W
IR
PT
Th Em
Ra Em
NT
0
VIII
IA
IB
IIA
IIB
IIIA
IIIB
IVA
IVB
VA
VB
VIA
VIB
VIIA
VIIB

Fig. 177

imaginary journey down the helix, beginning at the top. Hydrogen (atomic number and atomic weight = 1) stands by itself, and is followed by the first inert, zero group, and zero valent element helium. Here there comes the extremely sharp break in chemical properties with the change to the strongly positive, univalent element lithium, followed by the somewhat less positive bivalent element beryllium, and the third group element boron, with a positive valence of three, and a weaker negative valence. At the extreme right of the outer cylinder is carbon, the fourth group transition element, with a positive valence of four, and an equal negative valence, both of approximately equal strength. The first element on the back of the cylinder is more negative than positive, and has a positive valence of five, and a negative valence of three. The negative properties increase until fluorine is reached and then there is a sharp break of properties, with the change from the strongly negative, univalent element fluorine, through the zero valent transition element neon, to the strongly positive sodium. Thus in order around the outer loop the second series of elements are as follows: —

Group number.....	0	1	2	3	4	5	6	7
Maximum valence...	0	1	2	3	4	5	6	7
Element.....	He	Li	Be	B	C	N	O	F
Atomic number.....	2	3	4	5	6	7	8	9

"After these come neon, which is like helium, sodium which is like lithium, etc., to chlorine, the eighth element of the second period. For the third period the journey is continued, still on the outer loop, with argon, potassium, calcium, scandium, and then begins with titanium, to turn for the first time into the inner loop. Vanadium, chromium, and manganese, which come next, are on the inner loop, and thus belong, not to main but to sub-groups. *This is the first appearance in the system of sub-group elements.* Just beyond manganese a catastrophe of some sort seems to take place, for here three elements of one kind, and therefore belonging to one group, are deposited. The eighth group in this table takes the place on the inner loop which the rare gases of the atmosphere fill on the outer loop. The eighth group is thus a sub-group of the zero group.

"After the eighth group elements, which have appeared for the first time, come copper, zinc, and gallium; and with germanium,

a fourth group element, the helix returns to the outer loop. It then passes through arsenic, selenium, and bromine, thus completing the first long period of 18 elements. Following this there comes a second long period, exactly similar, and also containing 18 elements.

"The relations which exist may be shown by the following natural classification of the elements. They may be divided into cycles and periods as follows:

TABLE I

Cycle 1 = 4^2 elements.	
1st short period.....	He — F = 8 = 2×2^2 elements.
2nd short period.....	Ne — Cl = 8 = 2×2^2 elements.
Cycle 2 = 6^2 elements.	
1st long period.....	A — Br = 18 = 2×3^2 elements.
2nd long period.....	Kr — I = 18 = 2×3^2 elements.
Cycle 3 = 8^2 elements.	
1st very long period.....	Xe — Eka-I = 32 = 2×4^2 elements.
2nd very long period.....	Nt — U.

"The last very long period, and therefore the last cycle, is incomplete. It will be seen, however, that these remarkable relations are perfect in their regularity. These are the relations, too, which exist in the completed system,* and are not like many false numerical systems which have been proposed in the past where the supposed relations were due to the counting of blanks which do not correspond to atomic numbers. This peculiar relationship is undoubtedly connected with the variations in structure of these complex elements, but their meaning will not be apparent until we know more in regard to atomic structure.

"The first cycle of two short periods is made up wholly of outer loop or main group elements. Each of the long periods of the second cycle is made up of main and of sub-group elements, and each period contains one eighth group. The only complete very long period is made up of main and of sub-group elements, contains one eighth group, and would be of the same length (18 elements) as the long periods if it were not lengthened to 32 elements by the inclusion of the rare earths.

* If elements of atomic weights two and three are ever discovered then the zero cycle would contain 2^2 elements, and the first period should then be said to begin with lithium. Such extrapolation, however, is an uncertain basis for the prediction of such elements.

"The first long period is introduced into the system by the insertion of iron, cobalt, and nickel, in its center, and these are three elements whose atomic numbers increase by steps of one while their valence remains constant. The first very long period is formed in a similar way by the insertion of the rare earths, another set of elements whose atomic numbers increase by one while the valence remains constant.

"In this periodic table the *maximum* valence for a group of elements may be found by beginning with *zero* for the zero group and counting toward the front for *positive* valence, and toward the back for *negative* valence.

"The negative valence runs along the spirals toward the back as follows: —

0	−1	−2	−3	−4
Ne	F	O	N	C
A	Cl	S	P	Si

"Beginning with helium the relations of the maximum theoretical valences run as follows: —

Case 1. He–F.... 0, 1, 2, 3, 4, 5, 6, 7, but does not rise to 8. Drops by 7 to 0.
Ne–Cl... 0, 1, 2, 3, 4, 5, 6, 7, but does not rise to 8. Drops by 7 to 0.
Case 2. A–Mn... 0, 1, 2, 3, 4, 5, 6, 7, 8, 8. Drops by 7 to 1.
Fe, Co, Ni.
Case 1. Cu–Br.
Case 2. Kr–Ru, Rh, Pd.

"In the third increase, the group number and maximum valence of the group rise to 8, three elements are formed, and the drop is again by 7 to 1.

"Thus in every case when the valence drops back the drop in maximum group valence is 7, either from 7 to 0, or from 8 to 1. This is another illustration of the fact that the eighth group is a sub-group of the zero group. The valence of the zero group is zero. According to Abegg the contra-valence, seemingly not active in this case, is eight."

Structure of the Nucleus. As has already been pointed out in the preceding chapter, swift moving electrons and helium nuclei are ejected at various stages in the disintegration of the radioactive elements, uranium, thorium and actinium. Since the general property of radioactivity is peculiar to the nucleus alone, the emission of electrons and α-particles from uranium, thorium

and actinium has led to the view that the nuclei of these and other heavy atoms must be made up of both negative electrons and positively charged helium nuclei. It has also been assumed that the nucleus of the helium atom is in reality a secondary nucleus comprising four hydrogen nuclei and two electrons. If these assumptions are correct, it is reasonable to infer that the nuclei of all atoms are ultimately composed of hydrogen nuclei, or protons, and negative electrons. The property of radioactivity, therefore, not only furnishes a hint as to the possible structure of atomic nuclei, but also provides the means, in swift moving α-particles, with which to penetrate the hidden, inner structure of non-radioactive atoms. By bombarding the atoms of matter with α-particles and following the resultant deflections in their paths, Rutherford and Chadwick * have been able to ascertain the magnitude of the forces in the neighborhood of the nucleus and to form some idea of its dimensions. From an examination of the ejected particles, by measurements of their deflections in a magnetic field, these investigators have found that many of the elements suffer disintegration under α-ray bombardment with the emission of hydrogen nuclei.

The odd elements, boron, nitrogen, fluorine, sodium, aluminium and phosphorus, all give particles varying in range from 40 to 90 cm., while the even elements, carbon, oxygen, neon, magnesium, silicon and sulphur, either give few particles, or none at all, as in the cases of carbon and oxygen. The difference in the velocity with which the hydrogen nuclei are expelled from the nuclei of the odd and even elements is not without interest. Similar differences in the behavior of odd and even elements have been noted in other directions. Thus, Harkins found that elements of an even atomic number are much more abundant in the earth's crust than those of an odd atomic number, while Aston has pointed out that, in general, those elements having odd atomic numbers have only two isotopes differing in mass by two units, while elements having even atomic numbers often contain a large number of isotopes. Just what these differences signify, it remains for future research to reveal.

In this connection attention should be called to the hydrogen-

* Rutherford and Chadwick, Phil. Mag., vi, 44, 417 (1922); see also Rutherford's lecture, "The Artificial Disintegration of the Elements," Jour. Chem. Soc., 121, 400 (1922).

helium system of atomic structure discovered by Harkins and Wilson.* Beginning with helium, and adding 4 units of atomic weight for each increase of 2 units in the atomic number, gives the atomic weights of the elements in the even-numbered groups of the periodic table, neglecting small changes in mass due to nuclear packing. This rule has been found to hold very closely for all of the elements having atomic weights below 60.

The atomic weights of the elements of the odd-numbered groups can be calculated by a similar rule, provided that the atom of lithium, the first member of the odd-numbered groups, be assumed to be made up of 1 helium and 3 hydrogen nuclei. The following table gives the results, as calculated by Harkins and Wilson, for the first three series of the periodic table.

The so-called theoretical atomic weights are calculated on the basis H = 1, while the experimentally determined values are on the basis O = 16, or H = 1.0078. The remarkably close agreement between the two sets of values is taken as an indication that the packing effect, resulting from the formation of the elements from hydrogen nuclei and attendant electrons, is very small. This packing effect has been estimated to involve a decrease in atomic mass of about 0.77 per cent, and is believed to be due almost entirely to the formation of the helium atom. The hydrogen-helium hypothesis of atomic structure offers a rational explanation of many interesting but hitherto obscure facts concerning the nature of the elements.

From the experiments of Rutherford and Chadwick it is evident that the nuclei of even the lighter elements must be exceedingly complex structures. The failure to break up the atom of chlorine and the atoms of the heavier elements under α-ray bombardment may be ascribed to the fact that the nuclear charges of those atoms are so high that the energy of the impact of the α-particles is insufficient to effect disintegration.

While as yet the actual structure of atomic nuclei is largely a matter of conjecture, the work of Rutherford and Chadwick leaves no room for doubt as to the ultimate units of which that structure is composed.

Transmutation. Very closely connected with the subject of atomic disintegration is the problem of atomic transmutation. When an element undergoes disintegration, a unit charge is torn

* Harkins and Wilson, Proc. Nat. Acad., Vol. I, p. 276 (1915).

THE HELIUM — H_3 SYSTEM OF ATOMIC STRUCTURE. H = 1.0078.

	0	1	2	3	4	5	6	7	8	
At. No.	2	3	4	5	6	7	8	9		
	He	Li	Be	B	C	N	O	F		
Ser. 2...	He	He + H_3	2 He + H	2 He+H_3	3 He	3 He + H_2	4 He	4 He + H_3		
Theor...	4.00	7.00	9.0	11.0	12.00	14.00	16.00	19.00		
Det.....	4.00	6.94	9.1	11.0	12.00	14.01	16.00	19.00		
At. No.	10	11	12	13	14	15	16	17		
	Ne	Na	Mg	Al	Si	P	S	Cl		
Ser. 3...	5 He	5 He+H_3	6 He	6 He+H_3	7 He	7 He + H_3	8 He	8 He + H_3		
Theor...	20.0	23.0	24.00	27.0	28.0	31.00	32.00	35.00		
Det...	20.0	23.0	24.32	27.1	28.3	31.02	32.07	35.46		
At. No..	18	19	20	21	22	23	24	25	26	27
	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co
Ser. 4...	10 He	9 He+H_3	10 He	11 He	12 He	12 He+H_3	13 He	13 He + H_3	14 He	14 He+H_3
Theor...	40.0	39.00	40.00	44 0	48.0	51 0	52.0	55.00	56.00	59.00
Det.....	39.9	39.10	40.07	44.1	48.1	51.0	52.0	54.93	55.84	58.97

Increment from Series 2 to Series 3 = 4 He. Increment from Series 3 to Series 4 = 5 He (4 He for K and Ca). Increment from Series 4 to Series 5 = 6 He.

away from the nucleus of the atom. Any field of force tending to regain the lost charge is limited to the nucleus, and must contend with the enveloping field of force which tends to repel the lost charge. Unlike the loss of an electron by an atom, in the case of ionization — where the field of force surrounding the atom is of a sign which tends to attract the lost electron and thus restore the neutrality of the atom — the loss of a proton by the nucleus effects a permanent change. Therefore, it is quite reasonable to assume that if a proton could be removed from an atom of sodium (Na^{23}), for example, it would be possible to obtain an atom of neon (Ne^{22}) which, upon losing its excess electron, would be absolutely indistinguishable from any other atom of neon (Ne^{22}). In other words, if the process could be carried out, we should have effected the transmutation of sodium into neon.

Numerous attempts have been made to transmute one element into another ever since the era of alchemy, but up to the present time such experiments have been attended with little success. Recently Miethe and Stammreich* have claimed to have succeeded in transmuting mercury into gold. By the prolonged use of a mercury-vapor lamp, the mercury, which was known to be initially free from gold, was found to contain minute traces of the precious metal. The experiments of Miethe and Stammreich have quite recently been repeated with great care by Haber, Jaenicke and Matthias.† These investigators failed to secure any evidence of the transmutation of mercury into gold, notwithstanding the fact that they subjected the mercury to a much more intensive and prolonged electronic bombardment than that employed by Miethe and Stammreich.

The possibility of effecting the transmutation of mercury into gold is not at all improbable from the theoretical standpoint, since it merely involves the removal of one helium nucleus from the nucleus of the mercury atom, as indicated in the following scheme:

$$\text{Hg (201)} - \text{He (4)} = \text{Au (197)}.$$

Extra-nuclear Structure. While there is quite general agreement amongst both physicists and chemists that the atom possesses a nuclear structure and that the number of extra-nuclear

* Miethe and Stammreich, Zeit. anorg. Chem., **148**, 93 (1925); **149**, 263, (1925); **150**, 350 (1926).

† Haber, Jaenicke and Matthias, Zeit. anorg. Chem., **153**, 153 (1926)

electrons is equal to the atomic number, or the number of units of positive electricity associated with the nucleus, there is a wide divergence of opinion as to the manner in which the extra-nuclear electrons are arranged about the center of the atom.

The forces which hold the outer electrons in their orbits are believed to be comparatively weak, since some of the electrons can either be removed from, or restored to, the atom with the production of ions. A change in the number of the outer electrons does not give rise to any fundamental change in the character of the atom, but merely causes a change in valence.

The forces which govern the configuration of the extra-nuclear electrons are the resultant of the attraction of the nucleus and the mutual repulsion of the electrons themselves. Under the influence of certain external agencies, such as that of the electric field in electrolysis, the electrostatic forces can be overcome and one or more electrons split off from the atom. The amount of energy required to remove an electron from an atom is commonly known as the "ionizing potential." It is quite obvious that the outermost electrons can be more easily split off than those which are nearer to the nucleus of the atom. The outermost electrons are frequently referred to as "valence electrons." The configuration and behavior of the extra-nuclear electrons determine not only the optical and X-ray spectra of the atom, but also its other physical and chemical properties. The X-rays are associated with the electrons in close proximity to the nucleus, giving rise to the "K," "L" and "M" series of spectra.

There are today two hypotheses as to the configuration and behavior of the extra-nuclear electrons. One theory has been developed on the assumption that the electrons revolve in certain stable orbits around the nucleus, the selection of the orbits being governed by special hypotheses. This theory owes its inception and many of its applications to the Danish physicist, Niels Bohr. The atomic model of Bohr, which is based upon the original conception of Rutherford, is frequently referred to as the "dynamic atom model." Obviously an atom model in which the electrons are revolving in more or less complicated orbits is illy adapted to meet the requirements of the chemist in dealing with the phenomena of valence and chemical combination. To meet this need, a second hypothesis, known as the "static atom model," has been developed by Lewis, Langmuir and others. In this model, while

the electrons are assumed to be distributed in successive shells around the nucleus, they are also assumed to occupy certain fixed positions. The static atom model has proven useful in furnishing a clearer picture of molecular structure and also in connection with the interpretation of various chemical phenomena. In this connection Lewis says:

"If we regard as the important thing the orbit as a whole, and not the position of the electron within the orbit, and if each electron is assigned an independent orbit, then we may think of each electron orbit as having a fixed position in space. The average position of the electron in the orbit may be called the position of the electron, and will correspond entirely to that fixed position which was assigned in the theory of the static atom."

The Dynamic Atom Model. In 1913, Bohr* put forward a theory defining the orbits in which the electrons revolve around the nucleus of the atom. Starting with the atom of hydrogen as the simplest of all atoms, Bohr assumed it to consist of a minute positively charged nucleus around which, as a center, a single electron moves in a circular orbit. He made the additional assumption that the electron need not invariably traverse the same orbit, but may successively revolve around the nucleus in a number of fixed orbits at different speeds. He assumed that so long as the electron remains in any particular orbit it will not emit radiation, but that if it is displaced from one orbit to another, due to some thermal or electrical impulse, it will give out radiant energy as it changes its orbit. The frequency of the radiation which is dependent upon the difference in the kinetic energy of the electron in the two orbits may be computed by means of the quantum theory. In the case of the hydrogen atom, Bohr showed that the radii of the successive orbits in which the electron may revolve are in the ratio of the squares of the natural numbers, $1^2 : 2^2 : 3^2 : 4^2$, etc. He estimates that the radius of the innermost orbit in the hydrogen atom is 0.55×10^{-8} cm., while the radii of the successive orbits are four, nine, sixteen, etc., times this magnitude. The electron is estimated to revolve around the innermost orbit 6.2×10^{15} times in a second, which is equivalent to a velocity of 2000 meters per second. If we imagine the nucleus and the attendant electron of the hydrogen atom to be magnified in the same proportion, then when the diameter of the nucleus becomes 10 cm., the diameter of the electron will be 2 cm., and the radius of its

* Bohr, Phil. Mag., **26**, 1, 476, 857 (1913).

innermost orbit will be 1000 meters. It is quite apparent from these figures that the atom of hydrogen consists largely of empty space.

Bohr's theory involves three striking assumptions. The first assumption, to which we have already referred, is that the extranuclear electron of the hydrogen atom can revolve in any one of its different orbits without radiating energy. The second assumption is that of all the infinite number of orbits which may theoretically be assigned to the electron, only certain ones which are defined by the quantum hypothesis are actually possible. These so-called "stationary orbits" having been determined, can then be specified by the respective energies pertaining to them, as, for example, E_1, E_2, E_3, . . . E_n. Bohr's third assumption specifies the frequencies of the radiations which the atom containing certain stationary orbits is capable of emitting. Under the conditions which favor the emission of radiation, the electron is assumed to jump from an orbit of energy, E_n, to another orbit of lesser energy, $E_{n'}$, and as a consequence of this orbital displacement, an amount of energy, $E_n - E_{n'}$, is radiated. The frequency of the emitted radiation is given by the equation,

$$h\nu = E_n - E_{n'}, \tag{2}$$

where ν is the frequency and h is Planck's constant.

Assuming that Coulomb's law of inverse squares holds for the electrostatic attraction between the nucleus and the electron in the hydrogen atom, and making the further assumption that the angular momentum of the electron in each orbit is a multiple of $h/2\pi$, the energy corresponding to any orbit may be shown to be equivalent to

$$E_n = -\frac{2\pi^2 e^2 e'^2 m}{h^2} \cdot \frac{1}{n^2},$$

where e' is the charge on the nucleus and e the charge on the electron whose mass is m. Since in the hydrogen atom, $e' = e$, we obtain, on substituting in equation (2),

$$\nu = \frac{2\pi^2 e^4 m}{h^3}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right). \tag{3}$$

This equation reproduces with remarkable accuracy the frequencies of all of the principal lines of the hydrogen spectrum.

In 1885, Balmer pointed out that the wave-lengths of the lines in the hydrogen spectrum could be calculated by means of an empirical formula containing but a single arbitrary constant. This equation, commonly known as Balmer's formula, is generally written in the form

$$\lambda = A\frac{n^2}{n^2 - 4}, \tag{4}$$

where λ is the wave-length and n is any one of the series of natural numbers from 3 to 8. Each value of λ, therefore, corresponds to a single line of the spectrum; these different values taken together form a convergent series of wave-lengths of which the limiting value is $\lambda = A$. Since the frequency, ν, is obtained by dividing the velocity of light, c, by the wave-length, $\nu = c/\lambda$, and

$$= \frac{4c}{A}\left(\frac{1}{4} - \frac{1}{n^2}\right). \tag{5}$$

On comparing equations (5) and (3) they will be seen to be identical if we place $\frac{4c}{A} = \frac{2\pi^2 e^4 m}{h^3}$. It appears, therefore, that Balmer's formula is really a special form of the more general equation derived from Bohr's theory. The remarkable accuracy with which the frequencies of the lines in the hydrogen spectrum have been reproduced by Bohr's theory undoubtedly constitutes its greatest achievement up to the present time. It should be pointed out, however, that deductions from the theory relative to various other properties of hydrogen are not confirmed by experiment.

According to Bohr, the atoms of other elements possess a similar structure to that of hydrogen; that is, they are assumed to consist of groups of electrons moving in definite orbits around a central nucleus. As soon, however, as we come to consider the structure of helium, the next simplest atom to hydrogen, we find that there is difficulty in deciding whether its two extra-nuclear electrons move in the same, or separate, orbits. As we proceed to atoms containing a greater number of extra-nuclear electrons, the problem of configuration and orbital distribution becomes increasingly difficult of solution. We are almost forced to conclude, therefore, that, up to the present time, the quantitative success of Bohr's atomic

model is limited to the case of a simple nucleus with one attendant electron. In commenting on Bohr's theory, J. J. Thomson said: —

"It seems hardly likely that much progress can be made in the solution of the difficult problems relating to chemical combination by assigning in advance definite laws of force between the positive and negative constituents of an atom, and then on the basis of these laws building up mechanical models of the atoms."

While the Bohr theory has undoubtedly contributed to a clearer conception of the nature of atomic structure and has proven of great value to the physicist, especially in connection with the interpretation of spectral series, it cannot be said to have met the requirements of the chemist who is primarily interested in an atomic model which shall readily lend itself to the building of molecules and to furnishing a satisfactory conception of valence.

The Static Atom Model. In 1916, G. N. Lewis* formulated a theory of atomic structure in which the valence electrons were assumed to occupy fixed positions around a central nucleus. The salient features of this theory may be briefly summarized as follows:

(1) The atom of each element contains a central nucleus which remains unaltered during all ordinary chemical changes and which possesses a positive electrification corresponding to its position in the periodic table.

(2) The electrons surrounding the nucleus are arranged in concentric cubes, the outer cube, in the case of the neutral atom, containing negative electrons equal in number to the excess of positive charges on the nucleus.

(3) The number of electrons in the outer cube may vary between zero and eight.

(4) The atom tends to hold an even number of electrons in the outer cube, and especially to hold eight electrons symmetrically distributed at the eight corners of the cube.

(5) The cube of eight electrons is reached in the atoms of the rare gases, and this cube becomes, in a certain sense, the nucleus around which the larger cube of electrons of the next period is built.

(6) The electrons of an outer incomplete cube may be given to another atom, or enough electrons may be taken from other atoms to complete the outer group of eight electrons, thus accounting for positive and negative valence.

* Lewis, Jour. Am. Chem. Soc., **38**, 762 (1916).

A diagrammatic representation of the atoms ranging from lithium to fluorine is given in Fig. 178. It will be observed that the atom of lithium has one normal positive valence, represented by a single electron which is readily given up. The atom of fluorine, on the other hand, has one normal negative valence and seven contravalences; it can, therefore, take up another electron and thus complete its full quota of eight electrons. The resulting atom will then resemble the atom of neon, except that its nuclear charge will be smaller, and that the atom of fluorine has one negative charge whereas the atom of neon is neutral. If the seven

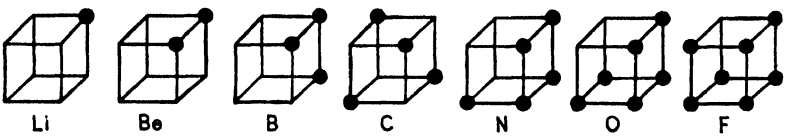


Fig. 178

electrons are removed from the atom of fluorine it will then resemble the atom of helium except for the difference in nuclear charge. The atom of each element can, therefore, be made, formally at least, to resemble the atom of one of the inert elements either by the removal or the addition of electrons.

A modification of the foregoing theory of the static atom has been developed by Langmuir * and is known as the "octet theory of atomic structure." In this theory it is assumed that the range of vibration of the electrons is so restricted that they may practically be considered as occupying stationary positions, symmetrically distributed about the atomic nucleus. It is also assumed, that the electrons are arranged in a series of concentric shells, the first of which contains two electrons, while the succeeding shells may contain as many as eight electrons. These eight electrons are assumed to distribute themselves singly at the corners of a cube, or in pairs at the corners of a regular tetrahedron.† In either case, the arrangement is assumed to be symmetrical.

The Periodic System and the Octet Theory. The periodicity of the properties of all of the elements, including the rare-earths and the members of the eighth group, can be satisfactorily ac-

* Jour. Am. Chem. Soc., 41, 868 (1919).

† It will be observed that Langmuir's "octet" is identical with Lewis's "group of eight."

counted for by the octet theory. Lack of space prohibits our giving more than a brief account of this interesting application of the octet theory. The classification of the elements according to the arrangement of their electrons is shown in the table given on p. 707, which will be seen to bear a close resemblance to the familiar periodic arrangement.

The Roman numerals in the first column denote the serial numbers of the outer shell of the atom, while the accompanying letters indicate the outside layer of this shell. The numbers in the second column represent the index number, and the subscripts to the symbols of the elements denote their atomic numbers. In order to find the number of electrons in the unfilled outside layer of the atom of any element, the preceding index number, given in the second column of the table, may be subtracted from the atomic number.

According to both the Lewis and the Langmuir theories an atom of an element having less than eight electrons in its outer shell, tends to acquire a sufficient number of electrons to complete its octet. Or, in case an atom has but few electrons in its outer shell, it tends to give up electrons to the atom of another element, thereby completing its octet. For example, the atom of lithium has only a single electron in its outer shell and, therefore, tends to complete the octet of the atom of some other element, such as fluorine, which lacks only one electron of a complete octet. The result of this redistribution of electrons is the formation of the compound, LiF.

In like manner, beryllium has two electrons, hence, by parting with one electron to each of two fluorine atoms their octets will be completed and the compound, BeF_2, will be formed.

The outer shell of the carbon atom lacks four electrons of a complete octet. In this case, the atom may either give up its four electrons, or acquire four extra electrons from some other atom, thereby completing its octet. For example, a carbon atom can give up its four electrons to each of two oxygen atoms, thus completing their octets and forming a molecule of carbon dioxide, or it can take up an electron from each of four hydrogen atoms, thereby completing its own octet, and forming a molecule of methane, CH_4.

Furthermore, if an atom is deprived of the opportunity of completing its octet at the expense of the atom of another element, it may share a pair of electrons with another atom of the same

CLASSIFICATION OF THE ELEMENTS ACCORDING TO THE ARRANGEMENT OF THEIR ELECTRONS

Layer	N	0	1	2	3	4	5	6	7	8	9	10
I			H_1	He_2								
IIa	2	He_2	Li_3	Be_4	B_5	C_6	N_7	O_8	F_9			
IIb	10	Ne_{10}	Na_{11}	Mg_{12}	Al_{13}	Si_{14}	P_{15}	S_{16}	Cl_{17}			
IIIa	18	A_{18}	K_{19}	Ca_{20}	Sc_{21}	Ti_{22}	V_{23}	Cr_{24}	Mn_{25}	Fe_{26}	Co_{27}	Ni_{28}
IIIa		$Ni\beta$	Cu_{29}	Zn_{30}	Ga_{31}	Ge_{32}	As_{33}	Se_{34}	Br_{35}			
IIIb	36	Kr_{36}	Rb_{37}	Sr_{38}	Y_{39}	Zr_{40}	Cb_{41}	Mo_{42}	(43)	Ru_{44}	Rh_{45}	Pd_{46}
IIIb		$Pd\alpha\beta$	Ag_{47}	Cd_{48}	In_{49}	Sn_{50}	Sb_{51}	Te_{52}	I_{53}			
IVa	54	Xe_{54}	Cs_{55}	Ba_{56}	La_{57}	Ce_{58}	Pr_{59}	Nd_{60}	(61)	Sa_{62}	Eu_{63}	Gd_{64}
IVa			Tb_{65}	Ho_{66}	Dy_{67}	Er_{68}	Tm_{69}	Tm'_{70}	Yb_{71}	Lu_{72}		
IVa		$Er\beta$	$Tm'\beta$	$Tm\beta$	$Yb\beta$	$Lu\beta$	Ta_{73}	W_{74}	(75)	Os_{76}	Ir_{77}	Pt_{78}
IVa		$Pt\beta$	Au_{79}	Hg_{80}	Tl_{81}	Pb_{82}	Bi_{83}	RaF_{84}	(85)			
IVb	86	Nt_{86}	(87)	Ra_{88}	Ac_{89}	Th_{90}	UX_{91}	U_{92}				

element. For example, two oxygen atoms may complete their octets by sharing a pair of electrons between them, thereby forming a single molecule of oxygen, O_2.

Turning now to the second period of the table, we begin with neon, which has a complete octet in its outer shell, and hence shows no tendency to give up, or acquire electrons. This is in complete accord with the well-known inertness of the element.

The next succeeding element is sodium, which should resemble its analogue, lithium, in the arrangement of its eleven electrons. Since two electrons are required to stabilize the nucleus, and eight more electrons are required to complete the first octet, it follows, that the remaining electron must become the first member of the next succeeding octet. The inner stable pair of electrons, and the electrons constituting the first octet, are without influence on the properties of the element. The sodium atom has no tendency to acquire seven other electrons, but readily gives up its one electron to complete the octet of the atom of some other element. In the event of its losing one electron, the atom of sodium will be left with a positive charge, and may be regarded as a free sodium ion.

The arrangement of the electrons in the outer shells of the remaining elements of the second period resembles that of their analogues in the first period. For example, the atom of silicon, like the atom of carbon, can either give up four electrons to complete the octet of the atom of some other element, or it can take up four additional electrons and thereby complete its own octet. The last element of the period, chlorine, has seventeen electrons, and by adding one more electron, the second octet will be completed, thereby again producing an arrangement of electrons which is characteristic of the inert gases. On referring to the table, we find that this new configuration of electrons corresponds to argon, the first member of the next period. In this manner the theory may be applied to the remaining elements in the table.

Electron Pairs and the Chemical Bond. In the development of their respective theories of the static atom, both Lewis and Langmuir have emphasized the tendency exhibited by the atoms of all the elements to complete their octets, or stable groups of eight electrons. Thus, in the formation of a molecule of sodium chloride from its constituent elements, each atom may be considered as completing its octet through the giving up of one electron by the sodium atom and the addition of one electron by the chlorine

atom. Lewis has pointed out, however, that this explanation of the mechanism of compound formation involves the unwarranted assumption that ionization invariably precedes combination, if each atom is to complete its full quota of eight electrons. As Lewis says: —

"The assumption of such ionization as a necessary accompaniment to all chemical combinations, even if it is assumed to be only 'intramolecular' ionization, leads to conclusions which are not reconcilable with the facts of chemistry."

In order to overcome this objection, he has proposed a new theory of combination between atoms which does not preclude the possibility of complete ionization. This theory may be stated in the following manner: — Two atoms may complete their groups of eight, or octets, not only by transfer of electrons from one atom to another, but also by sharing one or more pairs of their outer electrons. Lewis lays particular stress upon the importance of this conception of valence, and expresses his conviction that the "rule of two" is even more fundamental than the "rule of eight."

Such a pair of electrons, shared in common by two atoms, is considered by Lewis to constitute the chemical bond. Thus, for example, when two atoms of hydrogen unite to form a diatomic molecule, each atom is assumed to furnish one electron to form the bond which holds them together. If we represent a valence electron by a dot, the hydrogen molecule may be represented graphically by the formula, H : H. In like manner, when an atom of hydrogen with one electron unites with an atom of chlorine with seven electrons, the resulting molecule of hydrochloric acid will be represented by the formula, H : $\ddot{\underset{\cdot\cdot}{\text{Cl}}}$: . In this formula only the electrons in the outer shell of the chlorine atom are indicated. If it is desired to represent the complete chlorine atom with its nucleus and seventeen electrons, the molecule of chlorine will be depicted as shown in Fig. 179. When it is remembered, however,

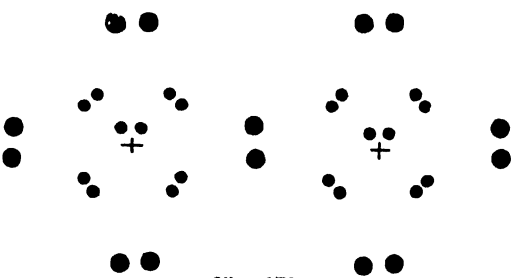
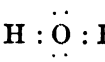


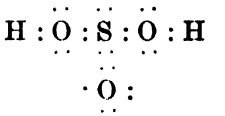
Fig. 179

that a two-dimensional diagram at best only suggests the actual spatial configuration of the electrons, it becomes evident that the simple diagrams in which the positions of the outer electrons alone are indicated will be sufficient. The following formulas, representing the constitution of a few typical molecules, will serve to familiarize the reader with the conception of the chemical bond as a pair of shared electrons:

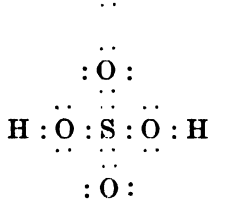
Water,



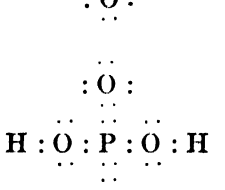
Sulphurous acid,



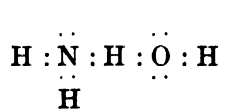
Sulphuric acid,



Phosphoric acid,



Ammonium hydroxide,



The conception of the chemical bond as a pair of electrons shared between two atoms furnishes a satisfactory explanation of the difference between polar and non-polar molecules. If the pair of bonding electrons is symmetrically placed between the two atoms which it joins, the resulting molecule will exhibit no polarity, but if the pair of electrons is not symmetrically placed, then one of the atoms will acquire a positive and the other a negative charge. For example, in the hydrogen molecule, the electron pair is probably symmetrically placed between the two hydrogen atoms and

the molecule is non-polar. In sodium hydride, however, the bonding pair is to be regarded as having undergone displacement in the direction of the hydrogen atom, making this negative and the sodium positive. In hydrochloric acid, on the other hand, the electron pair is displaced toward the chlorine atom, leaving the hydrogen atom positive and the chlorine atom negative. When hydrochloric acid is dissolved in a polar solvent, such as water, the chlorine atom completes its octet at the expense of the hydrogen atom, and the molecule of hydrochloric acid is ionized. The foregoing displacements of the bonding electrons may be represented graphically as follows:

$$H : H, \quad Na : H, \quad H : \ddot{\underset{\cdot\cdot}{Cl}} :, \quad [H]^+ + [: \ddot{\underset{\cdot\cdot}{Cl}} :]^-.$$

While in the molecule of hydrochloric acid, the hydrogen atom has its stable group of two, and the chlorine atom its stable group of eight electrons, there are, on the other hand, many molecules in which the simple process of sharing single pairs of electrons fails to bring about the completion of the stable octets of the atoms involved. As an example, the case of the oxygen atom may be cited. The atom of oxygen has only six valence electrons, and obviously if two atoms unite to form an oxygen molecule their octets will remain incomplete if only a single pair of electrons is shared between them. If, however, two pairs of electrons are shared, the full quota of eight electrons will be secured to each atom. In a union of this type, therefore, each atom is to be considered as located at the center of four electron pairs forming the corners of two tetrahedra which are joined at their apices. A convenient representation of this type of union is the following:

$$: O : : O :$$

In like manner, a triple bond may be represented by three pairs of bonding electrons, as for example in the molecule of acetylene,

$$H : C : : : C : H$$

Whatever may be the fate of the theories of atomic structure which have here been so briefly and inadequately outlined, — whether they be wholly rejected or radically modified as the result of further research, — it must be borne in mind that the experimental facts upon which these theories have been built are firmly

established and that they must furnish the basis for future advancement in our knowledge of the structure of matter.

"Who that once has seen
How truth leads on to truth, shall ever dare
To set a bound to knowledge?"

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